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Basaluminite and hydrobasaluminite, two new minerals from Northamptonshire.

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Introduction.

A WHITE mineral coating joint-faces in quarries in the Northampton ironstone (Inferior Oolite) was long ago recorded as allophane. W. D. Herman who determined the mineral from the surface of a sandstone rock in a quarry opened in 1871 also analysed an unnamed white earthy mineral from crevices in the ironstone and obtained a composition close to that of fully hydrated halloysite.

During the six-inch geological survey of that ironstone field in 1939–44 the occurrence of similarly situated white incrustations and joint infillings was found to be widespread especially in the shallow workings where the ferrous minerals chamosite and chalybite have been oxidized to produce a limonitic ore. In the large Lodge pit of the Irchester Ironstone Company, two miles south of Wellingborough the development of white mineral was much greater than had been observed elsewhere. Fissures up to one foot in width were largely filled with secondary white minerals and rock fragments. A preliminary optical examination by Dr. J. Phemister and X-ray photographs by Dr. G. Nagelschmidt had suggested the presence of more than one mineral in the white portion of the infilling.

A preliminary note recording the presence of two new minerals from Irchester was published in 1948. They are now described in more detail

and compared with related species in the British Museum. One of us (S. E. H.) has also added an account of the field relations and possible mode of origin.

Geological occurrence.

The Irchester pits lie in the south-eastern part of the ironstone field which includes the mines and quarries of the Finedon-Irthlingborough area to the north of the river Nene. This part of the field is the type area for the full lithological succession of the 'eastern type' of ironstone development (Hollingworth and Taylor, 1946). It has also provided much of the material on which recent advances in our knowledge of the petrology of the ironstone seam, and particularly of the lower and upper chamosite-kaolinite groups, have been made (Taylor, 1949). Amongst the changing physical and physico-chemical conditions during deposition that are revealed by variations in lithology and mineral content there is abundant evidence of penecontemporaneous secondary changes such as oxidation of ferrous minerals to limonite, of leaching processes, and of carbonatization. The formation of secondary sphaerosiderite, usually in the upper part of the seam and below a leached zone characterized by rootlets passing down from the overlying Lower Estuarine Series, may be mentioned.

The hydrated silicates and sulphates of aluminium which make up the white mineral of the Irchester fissures will be generally accepted as the products of oxidation and hydrolysis that are part of the weathering processes.

As they are found in the ironstone at Irchester beneath a cover of 60 feet or more of newer strata which includes impervious clays, the possibility arises that they may have been formed during a phase of weathering related to a Jurassic land surface. There is, however, as will be seen later, no evidence to support this view.

The present lie of the Northampton ironstone and overlying rocks on this part of Northamptonshire is attributable to two major factors: (i) the gentle regional dip, a fraction of one degree to the south-east, upon which has been superimposed, (ii) a pronounced local tilting of the strata that is closely related to the form of the ground and represents valleyward down-warping (cambering) or sagging of the strata. Concurrently with these movements new joint patterns were developed and subsidiary faulting occurred ('gulls' and 'dip and fault' structure). These movements have produced marked changes in the dip and altitude of the strata that locally completely mask the effects due to

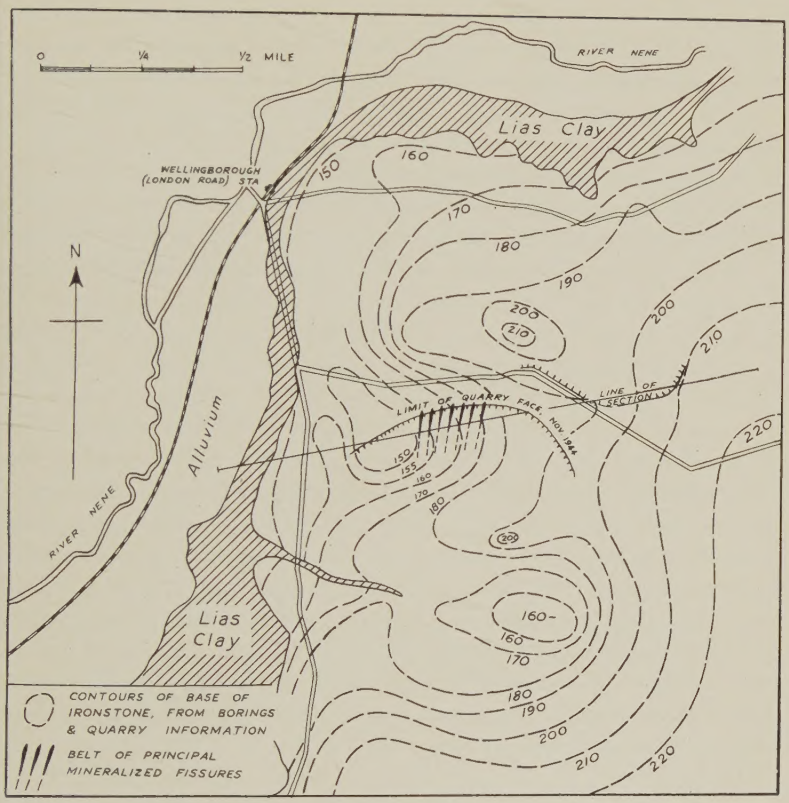

FIG. 1 *a*. Structure-contour map of Lodge pit area, Irchester, Northamptonshire.

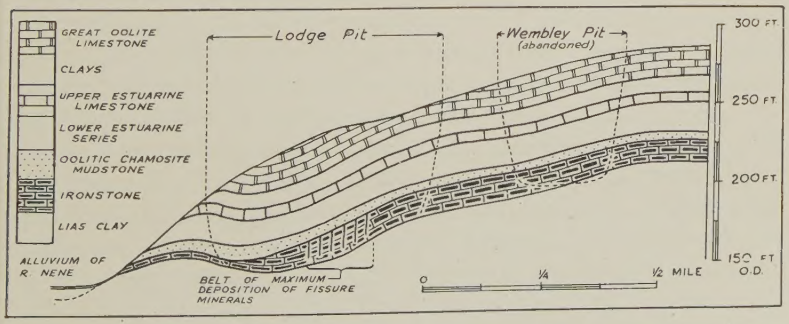

FIG. 1 *b*. Section across Lodge pit area.

the regional dip. The general principles that appear to apply to these movements have already been described (Hollingworth, Taylor, and Kellaway, 1944), and have been attributed to the valleyward flow of Lias clay causing disruption of the overlying massive beds from the Northampton Sand up to and including the Great Oolite limestone.

In some areas this valleyward down-warping is extremely uniformly developed on the valley side, with increasing inclination on the lower slopes. At other places, however, it is irregular in its development, due, perhaps, to strongly localized outflow of the Lias towards the valley (Hollingworth and Taylor, 1946, p. 229). Excellent examples of the structures produced by such movements are found in the Irchester area in the region that has been extensively bored and subsequently quarried by the Irchester Ironstone Company.

Fig. 1 shows the results of such movements as revealed by the structure contours drawn on the base of the Northampton Sand in the neighbourhood of Lodge pit. Somewhat elongated trough-like depressions opening out towards the valley, and with a rounded closed head towards the plateau are clearly displayed. In one case at least there is a strong suggestion that the depression or sag is an enclosed basin of small extent at its lowest point. The location of the infilled fissures which contain the minerals described below is indicated on this map. The possible significance of the location of these exceptional deposits of hydrated aluminium silicate and sulphate in this basin-shaped structure will be discussed later.

The deposits.

The mineral assemblage, including the two new minerals, occurs along joints as a coating on the wall-rock and as filling narrow fissures, or as matrix to the infilling in which there are variable amounts of broken or brecciated rock. Their occurrence compares with that of the mineralized fracture or lode which is typical of many metallic and non-metallic ore-bodies, and they show comparable evidence of a sequence of deposition and of movement along the fractures during the process of infilling. They clearly die out downwards, and were filled in from above (cf. some haematite ore-bodies). At Lodge pit the more important and wider fissures trend approximately N.–S. more or less normal to the working face as seen during the years 1941–8. Other open joints trending E.–W. have coatings of white mineral.

The greatest development of white minerals occurred in N.–S. fissures for some 300–400 yards east from the site of Little Irchester Lodge, the

buildings of which have since been obliterated by the northward advance of the quarry face. In this advance during 1945–8 the width of the fissures gradually decreased and their changing width is illustrated diagrammatically on fig. 1.

Fig. 2 is a composite sketch of a typical major N.–S. fissure. The fissures may be up to one foot wide, but seldom reach down to the base of the ironstone. In this aspect they contrast with the typical silt-filled fissures or 'gulls' described from the Pitsford ironstone quarry (Hollingworth, Taylor, and Kellaway, 1944).

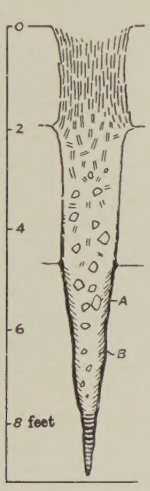
0
2
4
6
8 feet
A
B
Massive chalybite mudstone, with 'spalling' flakes of oxidized rock filling fissure.
Shelly chalybite-chamosite oolite. Fissure filled with the new minerals and allophane as matrix to flakes of oxidized chalybite mudstone and fragments of chamosite oolite.
Chalybite-chamosite oolite, with oolite fragments in white mineral matrix, largely of allophane. Walls coated with precipitated banded goethite (A), and banded allophane, &c. (B).
Lower part of fissure filled with laminated goethite mud.

Fig. 2. Diagrammatic section of typical fissure in ironstone.

The uppermost bed of the ironstone is a massive chalybite mudstone which weathers by the spalling off of thin plates, $\frac{1}{8}$–$\frac{1}{4}$ inch thick, of limonitized chalybite. This appears to have taken place as the fissure opened so as to occupy the space formed, for there is little infilling from above, and only thin coatings of white mineral on the major joints.

In the underlying shelly chalybite-chamosite oolite weathering has oxidized much of the massive joint blocks to ochreous brown limonitic stone with surviving cores of fresh green carbonate stone. An outermost skin to the joint blocks consists of dense dark brown limonite, clearly a secondary enrichment. Deposited on the latter where it forms the wall of a fissure there is usually a thin layer of fairly compacted brown goethite, $\frac{1}{8}$–$\frac{1}{4}$ of an inch thick, which becomes less prominent in the upper part of the fissure. This goethite shows a banded depositional

structure with minor unevenness due to development of small scale mamillation.

Following this goethite outwards is a second layer. This is usually fairly hard white and yellowish allophane, with well-defined banding consisting of fine alternation of translucent and opaque porcellaneous bands which are nearly vertical adjoining the goethite, but become less inclined away from it, dipping towards the centre of the fissure as if developing a catenary form of lamination. This deposit may be up to an inch thick, but is usually less. Its inner surface is frequently highly indented with small downwardly inclined projections resembling minute stalactites. Secondary fibrous gypsum, presumably of later date, is in places found between this deposit and the rock-wall. Calcite in masses the size of a small pin head, aragonite needles, and long hair-like gypsum crystals all occur locally as a later deposit on the 'allophane' in open fissures.

In some of the larger fissures goethite appears not only on the walls, but also as a finely laminated goethite clay filling the lower part of the fissure. It is a soft inconsolidated greasy clay, but may be contemporaneous with that higher up on the walls.

The central part of the infilling below the chalybite mudstone is a breccia of fragments of the wall-rock in a white matrix consisting of the new minerals basaluminite and hydrobasaluminite associated with allophane. In the upper part fragments are mostly limonitized chalybite mudstone, and in the lower part brown oolitic ironstone. Massive halloysite occurs immediately below the chalybite mudstone. There is some evidence that this assemblage is a late stage in the infilling which is usually preceded by the deposition of (1) goethite, (2) banded allophane.

Description of the Minerals. (F.A.B.)

The white infilling of the ironstone fissures includes a white compact mineral with conchoidal fracture and a white plastic clay-like mineral. The latter rapidly loses water in air and crumbles to a fine powder which does not regain its plastic character when wetted. For this reason several specimens were collected in damp cloths and kept in their original plastic condition by standing them in the upper chamber of a desiccator containing water. Associated minerals from the joints and fissures of the ironstone are gypsum, aragonite, halloysite, and a black manganese oxide gel mineral, an X-ray photograph of which shows only weak haloes, approximate spacings in Å.: 4·7, 3·12, 2·36, 2·20, 1·92, 1·62, 1·41.

Those specimens of the white plastic mineral which were allowed to dry at room-temperatures broke up and revealed inclusions of a compact pale yellow gel mineral identified as allophane with refractive index close to 1·48. The air-dried material is a fine-grained, powdery to compact substance consisting of minute birefringent plates or fibres with mean refractive index 1·519 and specific gravity 2·12. Powder

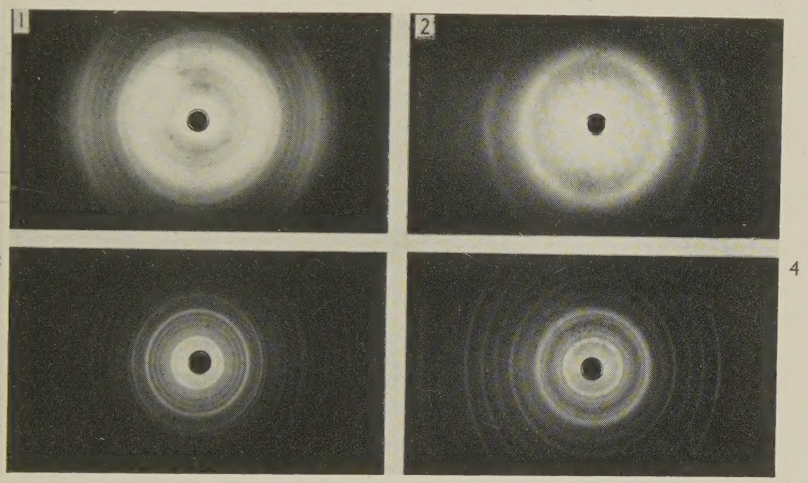

FIG. 3. X-ray powder photographs of: 1, hydrobasaluminite in a sealed lithium glass capillary tube; 2, allophane; 3, basaluminite; 4, metabasaluminite. Taken with filtered copper radiation, λ 1·5418 Å. in a cylindrical camera 6 cm. diameter.

photographs of a large number of air-dried samples containing the white mineral sometimes showed the presence of allophane haloes (fig. 3, no. 2; approximate spacings in Å.: 3·44 vs, 2·28 s, 1·86 w, 1·40 m, 1·23 w) and all gave the same line-rich pattern excepting for a marked variation in the intensity of the innermost line 12·6 Å. (see table I, cols. 1 and 2; fig. 3, no. 3). Specimens dried in air after powdering for longer periods yielded the same pattern, but with the 12·6 Å. line either very weak or completely missing. These preliminary photographs suggested that at least two minerals are present in the original samples, one of which in the moist state gives a strong X-ray diffraction that disappears when the mineral is dried in air.

A small quantity of the plastic material kept moist in saturated water vapour as described above was quickly packed into a fine capillary of lithium glass both ends of which were then plugged with wax. The

capillary was then mounted vertically and the powder photograph obtained (table I, col. 1; fig. 3, no. 1) was found to be quite different from that of the air-dried mineral (table I, col. 2; fig. 3, no. 3). It is above all characterized by the strong diffraction at 12·6 Å. The glass capillary was then unplugged and the plastic contents allowed to dry in air. A further X-ray powder photograph showed the pattern of the air-dried mineral and the pattern of the moist mineral had disappeared.

TABLE I. X-ray powder data for aluminium sulphate minerals.

1		2		3		4		5	
Hydro-basaluminite.		Basaluminite.		Meta-basaluminite.		Felsőbányite.		Aluminite.	
12·6 Å.	vvs	9·4 Å.	vs	8·5 Å.	vvs	4·58 Å.	m	9·0 Å.	s
8·08	m	7·18	vvw	6·90	ms	4·24	m	7·8	s
6·18	s	6·73	w	5·97	m	3·58	m b	6·33	ms
5·29	s	5·92	m	4·90	ms	3·1	ms b	5·4	m
4·70	s	5·27	m	4·36	vs	2·68	vw	5·2	vw
4·23	ms	4·68	s	4·14	ms	2·50	w	4·96	m
4·00	ms	3·87	m	3·72	vw	2·33	m b	4·7	ms
3·73	s	3·68	ms	3·46	mw	2·22	m b	4·18	m b
3·43	m	3·44	m	3·20	w	2·10	vw	3·72	s
3·21	w	3·20	vw	2·92	ms	2·00	vw	3·54	vw
3·07	s	2·90	w	2·76	w	1·910	mw	3·41	m
2·83	mw	2·82	w	2·68	w	1·734	w	3·31	w
2·57	m	2·71	mw	2·54	vw	1·729	vw	3·16	w
2·41	m	2·45	mw	2·48	m	1·685	vw	3·06	mw
2·25	m	2·38	vw	2·42	mw	1·625	mw	3·01	mw
2·22	w	2·26	m	2·30	vvw			2·86	w
2·10	ms	2·18	mw	2·19	m			2·68	mw
2·06	w	2·06	w	2·10	vw			2·60	vw
1·96	mw	2·02	w	2·02	vw			2·49	vw
1·835	ms	1·958	vw	1·921	s			2·38	vw
1·793	m	1·880	ms	1·851	w			2·32	vw
1·729	mw	1·835	mw	1·753	w			2·19	mw
1·680	vw	1·762	mw	1·689	mw			2·13	vw
1·625	ms	1·678	vw	1·665	w			2·08	vw
1·560	vvw	1·616	mw	1·602	mw			2·048	vw
1·500	w	1·601	w	1·560	w			1·960	mw
1·445	m	1·462	vw	1·518	w			1·908	vw
1·408	vw	1·448	vw	1·485	vw			1·879	vw
1·382	vw	1·433	m	1·458	ms			1·840	vw
1·349	vw	1·414	vw	1·426	ms			1·810	vvw

1. Hydrobasaluminite, $Al_4SO_4(OH)_{10}.36H_2O$: white plastic clay-like material from Lodge pit, Irchester, Northamptonshire. A portion of this specimen dried in air yielded basaluminite (no. 2 following).

2. Basaluminite, $Al_4SO_4(OH)_{10}.5H_2O$ (analyses 1 and 2, table II): white, powdery to compact substance consisting of minute birefringent plates or fibres with mean refractive index 1·519 and specific gravity 2·12. These data are also given by basalu-

minite from Épernay, Marne, France (analysis 3, table II) and by the same mineral from Clifton Hill, Brighton.

3. Metabasaluminite, $Al_4SO_4(OH)_{10}$: produced by heating hydrobasaluminite or basaluminite at 150° C. n 1·523, sp. gr. 2·20.

4. Felsőbányite: yellowish concretions on stibnite, Felsőbánya, Szatmár, Hungary (= Baia Sprie, Romania).

5. Aluminite: grey-white nodular massive, Newhaven, Sussex.

The above data were obtained from X-ray photographs of powdered specimens 1–5 with filtered cobalt radiation λ 1·7902 Å. in a cylindrical camera, 6 cm. diameter. Relative intensities are given as: vs very strong, s strong, ms medium strong, m medium, mw medium weak, w weak, vw very weak, vvw very very weak. See also fig. 3 for reproductions of powder photographs.

X-ray powder spacings given for basaluminite from Irchester by Bassett and Goodwin (1949, p. 2278) correspond to a mixture of hydrobasaluminite and basaluminite.

Air-dried material was then selected for chemical analysis. Both microscopic and X-ray examination were carried out to check that allophane was absent. Mr. Harvey's analyses of two separate portions, table II, cols. 1 and 2, show that it is difficult to select a sample quite free from small amounts of allophane and no doubt traces of other minerals may also be present. The results of chemical analysis show that the principal mineral constituent is a basic aluminium sulphate with composition close to $2Al_2O_3.SO_3.10H_2O$. X-ray powder spacings (table I), chemical analyses (table II), refractive index, and specific gravity distinguish the mineral from aluminite $Al_2O_3.SO_3.9H_2O$. It can also be distinguished from other known minerals of similar composition. In order to convey an idea of its chemical nature and at the same time to differentiate it from aluminite, the name *basaluminite* is proposed for the air-dried mineral and *hydrobasaluminite* for the fully hydrated plastic mineral (table I, col. 1).[1]

Attempts to obtain dehydration data for the hydrobasaluminite were not completely successful. Portions of the mineral were kept at 16° C. in air of known water-vapour pressure until constant in weight by placing the mineral under cover with a beaker containing sulphuric acid of known dilution. It was found difficult to achieve equilibrium and bring samples to constant weight in a reasonable time. The outer layers of less hydrated material appear to form impermeable crusts which hinder the dehydration of the interior. The following measurements

[1] In the preliminary account of both minerals, already published, the values quoted for the longest spacings, 12·9 Å. for hydrobasaluminite and 9·2 Å. for basaluminite, are in error. More accurate measurements give 12·6±0·2 Å. and 9·4±0·1 Å. respectively. F. A. Bannister and S. E. Hollingworth, Nature, London, 1948, vol. 162, p. 565.

TABLE II. Chemical analyses of basaluminite.

	1.	1 a.	2.	2 a.	3.	4.	5.
SiO_2 ...	2·4	—	3·6	—	—	—	—
SO_3 ...	15·6	17·4	14·2	16·9	20·06	17·2	23·37
Al_2O_3...	43·0	43·5	41·3	42·2	39·70	44·0	29·87
Fe_2O_3...	0·3	—	0·2	—	—	—	—
P_2O_5 ...	trace	—	1·0	—	—	—	—
H_2O ...	(38·7)	39·1	(39·7)	40·9	39·94	38·8	46·76
	100·0	100·0	100·0	100·0	99·70	100·0	100·00
Sp. gr.	2·12		2·12		1·670		1·7054

1 and 2. Air-dried samples of basaluminite from Lodge pit, Irchester, Northamptonshire, containing up to 15 % allophane. Analysed by Mr. C. O. Harvey, Geological Survey Chemical Laboratory; water content by difference. Nature, London, 1948, vol. 162, p. 565. [M.A. **10**–452.]

1 a and 2 a. Recalculated excluding allophane.

3. Basaluminite, Mount Bernon, Épernay, Marne, France. Analysed by J. L. Lassaigne who determined each constituent separately and also found 0·30 % of calcium sulphate. Ann. Chim. Physique, Paris, 1823, ser. 2, vol. 24, p. 97.

4. Calculated for $2Al_2O_3.SO_3.10H_2O$.

5. Aluminite, Newhaven, Sussex, analysed by F. Stromeyer who determined each constituent separately and corrected for a small amount of admixed gypsum. Untersuchungen über die Mischung der Mineralkörper. Göttingen, 1821, p. 99.

were made, showing that the approximate composition of the fully hydrated hydrobasaluminite is $2Al_2O_3.SO_3.41H_2O$.

Total loss of weight.	Temperature degrees C.	Duration hours.	Mineral present.
0	16	—	hydrobasaluminite
52·9	16	120	basaluminite
54	16	240	basaluminite

No further loss in weight could be detected for the mineral at 16° C., but on raising the temperature further loss of water occurred and powder photographs were taken of the products obtained:

65·1	150	2	metabasaluminite
72·4	500	2	amorphous
73·6	750	2	amorphous
77·9	920	2	unidentified

No change in the powder pattern of basaluminite could be detected in samples heated to 105° C., but at 110° C. a change in pattern was observed that is apparently complete at 150° C. when the pattern remains constant and the chemical composition corresponds to $Al_4SO_4(OH)_{10}$ (table I, col. 3; fig. 3, no. 4). No further change in the powder pattern occurred when samples were heated to 200° and 300° C. At the latter temperature, however, the pattern begins to fade away and at 500° C. completely disappears, the material having become amorphous. The product

obtained by heating basaluminite to 750° C. is also amorphous and X-ray photographs show only haloes: approximate spacings in A. 3·7 s, 2·18 w, 1·46 w. When the amorphous product obtained at 750° C. is heated to 920° C. further loss in weight takes place possibly due to evolution of sulphur trioxide as well as water vapour and the X-ray photograph no longer shows haloes but powder lines flecked with spots, none of which can be attributed to either α- or γ-alumina. So far this recrystallized material has not been identified.

An X-ray examination has also been made of samples of the white minerals collected from Irchester by Dr. G. Nagelschmidt in 1943 and kindly lent to us for study. Most of them prove to be mixtures of basaluminite and allophane, but a few samples have been encountered which yield unidentified X-ray patterns suggesting the presence of additional, possibly undescribed, minerals that need further study.

Basaluminite yields a powder photograph with sharp, well-defined lines showing that the average crystal size is less than 5 μ - 5×10^{-4} cm. So it is not surprising that the optical data are meagre and that no optic picture can be obtained to show whether the mineral is uniaxial or biaxial. An attempt, however, has been made to index the first twelve lines of the basaluminite pattern, table I, col. 2, by using charts of the Hull-Davey type prepared by C. W. Bunn who has plotted values of log d for each possible crystal plane against log c/a for tetragonal, hexagonal, and rhombohedral substances. A satisfactory 'fit' could be obtained by using an hexagonal chart for an axial ratio c/a 0·8318:

d.	log d.	Indices.	d.	log d.	Indices.
9·4 Å.	0·9722	0002	3·87	0·5877	$41\bar{5}2$
7·18	0·8501	$11\bar{2}2$	3·68	0·5658	$10\bar{1}5$, $42\bar{6}0$, $33\bar{6}1$
6·73	0·8280	$20\bar{2}2$	3·44	0·5366	$42\bar{6}2$, $51\bar{6}1$
5·92	0·7723	$10\bar{1}3$	3·20	0·5051	$60\bar{6}1$, $43\bar{7}0$, $33\bar{6}3$
5·27	0·7218	$20\bar{2}3$	2·90	0·4624	$42\bar{6}4$
4·68	0·6702	0004, 3142	2·82	0·4502	$44\bar{8}0$, $30\bar{3}6$

This possible solution should not be taken too seriously, neither can we regard it as a proof that the symmetry of basaluminite is hexagonal. It is now possible to calculate the unit-cell dimensions and contents, but we must again emphasize that they are reported here only as a possible solution. The spacings of the two lines $44\bar{8}0$ and 0004 yield values of a 22·56, c 18·72 A and this hexagonal rhomb-based unit cell would contain $22{\cdot}72[2Al_2O_3.SO_3.10H_2O]$. It is always difficult to measure accurately the specific gravity of a porous fine-grained mineral and the approximate value 2·12 obtained during this work by immersion in a mixture of methylene iodide and benzene containing indicators of

known specific gravity is probably low. If it be assumed that the unit cell really contains an integral number of formula weights consistent with hexagonal symmetry, i.e. $24[2Al_2O_3.SO_3.10H_2O]$, the calculated specific gravity would be 2·23. The powder pattern of hydrobasaluminite is more complex than that of basaluminite, so that still less reliance could be placed on a graphical method of indexing its powder pattern.

Mention has already been made of the difference in chemistry, optical properties, and powder patterns of the new minerals from Irchester and aluminite proper. During the comparison of basaluminite with all possibly related aluminium sulphate species in the British Museum collections it was soon discovered that those specimens labelled aluminite revealed considerable variation in external characters, and X-ray photographs grouped them into three divisions each corresponding to a specific powder pattern:

1. Aluminite: grey-white, finely fibrous, nodular groups and masses (table I, 5). Localities represented: Halle, Germany; Newhaven, Sussex.

2. Basaluminite: white, powdery to compact, sometimes nodular (table I, 2) from Irchester, Northamptonshire, and Clifton Hill, Brighton, Sussex; also as white pellets up to 5 mm. long in a matrix of metahalloysite and fine-grained quartz from Épernay, Marne, France.

3. Gibbsite+allophane:[1] white, compact nodules consisting of an intimate mixture of the two minerals, from Clifton Hill, Brighton, Sussex. So-called collyrite from Hove, Brighton, should also be included here. A polished specimen in the British Museum collections showing concentric zones yields a sharp pattern due to gibbsite with a background of haloes due to allophane. It is of interest that the chemical analysis by J. H. and G. Gladstone corresponds, as J. D. Dana pointed out, to a composition equivalent to a mixture of equal parts of gibbsite and allophane.

The powder patterns of basaluminite from Irchester, Épernay, and Brighton are identical. This fact is good evidence that the pattern itself corresponds to one single mineral species. The 12·6 Å. line of hydrobasaluminite appearing on powder photographs of imperfectly dried basaluminite also appears on photographs of the interior of the white pellets from Épernay. Thus the outer crust of basaluminite can effectively

[1] A duplicate specimen of gibbsite, probably from Brighton, but incorrectly labelled aluminite, Newhaven, was used for the data on aluminite supplied to the American Society for Testing Materials for the first supplementary card file of X-ray data, 1944, A.S.T.M. II–356.

seal up the more hydrated mineral hydrobasaluminite for a long time. Table II, col. 3 shows the analysis of the Épernay mineral studied by J. L. Lassaigne. He pointed out the higher alumina and lower sulphate contents compared with aluminite specimens from Halle and Morl, but did not apparently suspect that he had analysed a new mineral species. So far this is the only known occurrence of basaluminite free from allophane. It would not, however, be easy to isolate sufficient white pellets for chemical analysis. Basaluminite from Clifton Hill, Brighton, formerly labelled aluminite, is, like the mineral from Irchester, frequently associated with allophane. No chemical analysis of the Brighton mineral has yet been published and its identification with basaluminite depends entirely upon X-ray photographs.

The relationship of the new minerals hydrobasaluminite and basaluminite to the doubtful species felsőbányite and paraluminite is still uncertain. No paraluminite from Halle is available for comparison, but the optical properties reported by Larsen (1921) do not suggest identity with basaluminite. The only specimens of felsőbányite in the British Museum that were not wrongly labelled are almost amorphous and yield only weak patterns quite different in spacings and relative intensities from the patterns for the two new minerals (table I, col. 4).

In a recent study of the basic aluminium sulphates by H. Bassett and T. H. Goodwin attempts to prepare basaluminite and hydrobasaluminite have failed. Their experiments were carried out at 25° C. or higher temperatures, and it is possible that attempts made at lower temperatures might be more successful. They have also published (1949, p. 2265) analyses of two specimens of basaluminite supplied by us from Northamptonshire and obtained a formula for basaluminite close to $2Al_2O_3.SO_3.10H_2O$. Bassett and Goodwin (p. 2265) state correctly that 'aluminite has not, so far, been found in the Northampton deposits'. They are in error, however, in stating (pp. 2252, 2265) that basaluminite is associated with aluminite on many specimens of that mineral: I have not detected it on any of the British Museum specimens of aluminite $Al_2O_3.SO_3.9H_2O$ from Halle or Newhaven (p. 12).

Although both the new minerals are basic aluminium sulphates, not aluminosilicates, they nevertheless show some relationship to members of the clay family: the difference in their longest powder spacings is 3·2 Å. and possibly corresponds as in halloysite and metahalloysite to the thickness of a water-layer in their layer structures. Fully hydrated halloysite with its longest spacing close to 10 Å. is more frequently encountered in the clay deposits of northern Europe,

whereas metahalloysite with composition close to that of kaolinite and longest spacing 7 Å. is the more usual form recorded in warmer climates. Halloysite readily passes into metahalloysite by heating to 70° C. Hydrobasaluminite is an example of a plastic mineral which can only be preserved indefinitely in a moist environment; and it may well be, if suitable precautions are taken in the collection and preservation of clays and other clay-like substances, that new hydrated forms of known minerals may be discovered.

Conditions of formation.

It is generally accepted that the breakdown of complex alumino-silicates by hydrolysis takes place in the zone of weathering, and the mobility of alumina and silica which is required for the transport of the constituents of the white mineral assemblage may be assigned wholly or in part to some such chemical breakdown. Although the presence of kaolinite in unweathered ironstones should not be overlooked, the association of the white mineral assemblage with the zone of weathering (but well below the present surface) is too intimate to be fortuitous. Sulphates of aluminium suggest the solution of alumina by acid waters derived from the oxidation of pyrite which is a widespread constituent of the unweathered ironstone. Pyrite is in places concentrated at the base of the upper chamosite-kaolinite group, and also occurs as a secondary deposit below the leached zone associated with the Lower Estuarine seat-earth.

It is not to be expected that the acidity or alkalinity of solutions derived from the zone of weathering will necessarily survive unmodified during their movement downward through varying environments. In particular, contact of acid alumina-bearing solutions with alkaline waters (e.g. of calcium bicarbonate derived from calcium carbonate in the ironstone or indirectly from the Great Oolite limestone) could lead to a precipitation of gypsum and then of alumina and silica gel (Clarke, 1920, p. 495). It has also been suggested by van Bemmelen (1904; Robinson, 1936, p. 45) that the colloidal sols of electro-negative silicic acid and electro-positive alumina and iron may cause mutual precipitation, first as adsorption compounds of indefinite composition giving rise later to crystalline compounds with definite composition. The general character of the central infilling—the halloysite-allophane-hydrobasaluminite assemblage is not inconsistent with crystallization from such an adsorption complex.

It is, however, difficult to visualize the accumulation of such large

quantities of material from presumably dilute solutions except under some specially favourable conditions. The basin-like structure suggested by fig. 1 would not sufficiently restrict circulation for continued precipitation. There is, however, some probability of a special combination of circumstances which could have produced unusually favourable conditions. This seems an appropriate place to mention these.

There are various facts, which it is hoped to describe in detail elsewhere, that point to an intimate, probably causal, relation between cambering and its associated superficial structures, and the abnormal conditions of the glacial climate of the Pleistocene. The suggestion that the partial or complete thawing of a deep zone of 'permanently frozen' ground could produce conditions favourable to development of superficial disturbances has already been made (Hollingworth, Taylor, and Kellaway, 1944, footnote p. 18). This receives support from the observations of Záruba-Pfeffermann (1943) in Czechoslovakia. Deeply frozen ground in the peri-glacial areas of southern Britain is favoured by Dr. A. J. Bull to account for the shattering of chalk, without appreciable mass movement, so as to preserve the lines of flint nodules such as he has observed in the Beachy Head area (personal communication), and can be well seen at Freshwater Bay in the Isle of Wight.

With these preliminary remarks we may refer to observations of Livingston Wernecke (1932) in the Yukon Territory where mining operations have proved frozen ground to a depth of more than 400 feet. Small ice veins (frozen ground-water) are abundant in the rock, and ice-rock breccia provides evidence of the splitting off of fragments from the walls of joints. Mine water contains 178 parts per million of solids mostly $CaCO_3$.

'When the underground water froze, the calcium carbonate seems to have segregated and precipitated in spots as a soft, white, pulverulent (when dry) mass on the walls of the fractures. When wet, this substance is a soft, pasty mass. Some of this material was observed included as small irregular-shaped masses in the ice, but the greater portion was on the edges of the ice. The carbonate was pronounced in the ice in the siderite veins, and not evident in the ice surrounded by slate or quartzite. In the last instance, a very thin coating of limonite has precipitated on the slate or quartzite walls.' (Wernecke, 1932, p. 43.)

This description of the occurrence of calcium carbonate has a striking resemblance to the occurrence of 'rock-milk', a soft deposit of fine-grained white calcium carbonate that is frequently found coating the joints in Jurassic limestones of the Cotteswolds and elsewhere.

Of the Chipping Norton limestone, H. B. Woodward wrote (1894, p. 149):

'In many quarries the exposed faces of the beds become lime-washed or incrusted with a calcareous coating. This is the "Rock Milk" (*Lac Lunae*) of old mineralogists, sometimes also termed the "Agaric Mineral" from its supposed resemblance to fungoid growth. The beds are often much shattered, and the "rifts" or "swillies" are filled with clay and débris from the overlying Great Oolite Series.'

Weaver (1824) wrote:

'Inferior oolite; traversed by fissures of variable width, the walls of which are frequently coated with rock-milk. . . .'

Wernecke's record of precipitated limonite is of particular interest in view of its occurrence in the fissures in the ironstone. We envisage a deeply-frozen ground in Northamptonshire during cold phases of the Pleistocene, with probably major and minor oscillations in the lower limit of freezing.

At the Lodge pit site the geological conditions are particularly favourable to the sealing up of a considerable volume of ground-water as freezing proceeded from above downwards. Freezing to a depth of say 10–15 feet would seal off the route of possible valleyward escape of ground-water on the valley sides, by freezing the ironstone outcrop down to the Lias clay, as may be seen from a consideration of fig. 1. At this stage ground-water could continue to feed down dip into the 'basin' area for some time with consequent accumulation and concentration of the silicates and sulphates of alumina, &c., as freezing proceeded. It is probable that the zone of frozen ground extended downwards through the ironstone into the Lias below.

The distribution of minerals in the fissures is suggestive of a precipitation succession –limonite, allophane, hydrobasaluminite; a sequence which may perhaps be regarded as a natural one.

One result of the weathering of the chalybite-chamosite ironstone is an increase in the silica-alumina ratio in the weathered rock (after allowance is made for free quartz originally present) (Taylor, 1949, pp. 55–56). It seems probable that the alumina-rich minerals of the fissure infilling represent nature's trapping of the soluble products of weathering. If this is so it would appear to provide useful information on the nature of the solutions derived from the weathering process in this particular environment, but the alumina/silica ratio of the deposit is much higher than is considered normal for the mobile products of weathering.

We should like to record our thanks to the Director of the Geological Survey who kindly gave his permission for publication of Mr. C. O. Harvey's analyses, to Dr. M. H. Hey for helpful discussions and advice, and to Dr. H. P. Stadler, then working in the Mineral Department of the British Museum, who carried out the measurements on dehydration and prepared many of the X-ray powder photographs. We would also express our indebtedness to Mr. Walter Woof, the manager at Lodge pit, for facilities for field collecting.

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Postscript.—The thin plates or fibres of basaluminite from Irchester have negative elongation and refractive indices in sodium-light n_1 1·517, n_2 1·521, yielding the average value 1·519 given above (pp. 7–8). The same mineral from Épernay and Brighton yields less distinct fibres and the mean refractive index recorded for sodium-light is 1·515. Preparations of metabasaluminite retain the fibrous appearance and negative elongation of basaluminite and have n_1 1·521, n_2 1·524, yielding the mean value 1·523 as given on p. 9.

Baryte-bearing nodules from the Middle Lias of the English east midlands.[1]

(With Plate I.)

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With a chemical analysis by C. O. Harvey, B.Sc.

[Read November 25, 1948.]

Introduction.

THE Middle Lias of Rutland, east Leicestershire, and north-west Northamptonshire was described by Judd[2] in 1875 as comprising an upper ferruginous member—the Marlstone Rock Bed—and a lower argillaceous division of blue clays, often micaceous or sandy, and carrying bands of 'septaria' and of 'ironstone balls'. In the septaria he recorded the occurrence of 'specular-iron, zinc-blende and pyrites'.

During the six-inch survey of one-inch New Series sheets 157 (Stamford) and 171 (Kettering) together with the adjacent parts of sheets 156 (Leicester) and 170 (Market Harborough) a considerable area of the lower argillaceous division was mapped. These beds, about 50–80 feet in thickness, and belonging to the *margaritatus* zone can be broadly separated into an upper series of fine micaceous blue-grey silts and silty clays and a lower series of blue-grey clays. In both members the nodules described by Judd are of common occurrence. In the northern and central parts of the area under consideration the upper subdivision of silts and silty clays is succeeded by the ferruginous limestones and oolitic ironstones of the Marlstone Rock Bed (*spinatum* zone): over much of the southern part, however, the Rock Bed is absent.

Exposures in the Middle Lias silts and clays are poor. Sections described by Judd at a few small brickyards, such as those near Whissendine in Rutland and Owston and Billesdon in Leicestershire, are now almost completely obscured. Exposures are to-day almost wholly confined to small sections on the banks of the brooks and streams tributary to the rivers Welland and Eye.

[1] Published with the permission of the Director of H.M. Geological Survey.

[2] J. W. Judd, The Geology of Rutland. Mem. Geol. Surv., 1875.

Nature and occurrence of the nodules.

Fine-grained carbonate nodules occur throughout the *margaritatus* zone both as discontinuous bands and as apparently isolated nodules. The horizontal spacing between individual nodules is very variable from less than a foot up to several yards. In the limited exposures available it is not possible to establish any relation between horizontal spacing of the nodules within a band and the vertical spacing of successive bands, as has been done for the Lower Lias of the Dorset coast by Lang, Spath, and Richardson.[1]

The nodules have a more or less flattened ellipsoidal shape. The ratio of the horizontal diameter to the vertical diameter is commonly between 2:1 and 3:1. Exceptionally it is as high as 4:1. As recorded by Tomkeieff[2] in the case of clay-ironstone nodules from the Coal Measures, the degree of flatness is greater in the larger nodules and the tendency is for small nodules to approach the spheroidal. The largest of the *margaritatus* zone nodules to be observed had maximum and minimum diameters of 16 inches and 4 inches respectively. In many exposures bedding planes and laminations in the Liassic silts and clays are not sufficiently obvious for their relation to the nodules to be determined. Wherever such planes are clearly distinguishable they are conformable to both the upper and lower surfaces of the nodules (text-fig. 1).

Two types of nodules are readily recognizable. The majority are of 'cementstone' type, fine-grained, pale to medium grey calcite mudstones reacting freely with cold dilute acid. Others confined largely to bands in the lower part of the zone are of 'clay-ironstone' type and consist of fine-grained iron carbonate. They are readily distinguishable from the cementstone nodules by reason of their darker grey to grey-brown colour, higher specific gravity, and resistance to dilute acid. Apart from such differences, due to the character of the carbonate present, the structure of the nodules both in hand-specimen and thin section appears to be identical. The majority of the nodules show a partially weathered and exfoliated outer skin and a central portion in which irregular septarian cracks are developed. No traces of lamination within the nodules are visible. In thin section they are seen to consist of turbid carbonate of average grain-size 0·005–0·015 mm. Through this

[1] W. D. Lang, L. F. Spath, and W. A. Richardson, Shales with "beef", a sequence in the Lower Lias of the Dorset coast. Quart. Journ. Geol. Soc. London, 1923, vol. 79, pp. 47–99. [M.A. 2–535.]

[2] S. I. Tomkeieff, On the occurrence and mode of origin of certain kaolinite-bearing nodules in the Coal Measures. Proc. Geol. Assoc. London, 1927, vol. 38, pp. 518–547. [M.A. 3–555.]

discoloured and often nearly opaque groundmass are scattered quartz grains, 0·05–0·1 mm. across and often marginally replaced by the carbonate, granular pyrite, a few flakes of white mica, occasional grains of alkali-felspar, and a varying amount of interstitial pale yellow-brown clay. Digestion of two nodules, one clay-ironstone, the other cementstone, in hot 10 % hydrochloric acid yielded insoluble residues of 10·7 %

Text-fig. 1. Chalybite mudstone nodule from *margaritatus* zone clays, bank of river Welland, 1200 yards NE. by N. of church at Rockingham, Northants. Nodule shows some exfoliation consequent upon weathering. Deformation of the bedding of the Lias clays both above and below the nodule is visible.

and 28·0 % respectively. The extremely fine-grained clay constituents of these residues are difficult to identify optically. Some kaolinite appears to be present associated with material of higher birefringence (approx. 0·011). X-ray examination of one of the residues by Dr. G. W. Brindley suggested the presence of both a kaolin-type and a mica-type clay, probably in comparable proportions.

An analysis of one of the iron carbonate nodules from an exposure in the banks of a brook, 1150 yards ESE. of Whissendine station, Rutland, was carried out by Mr. C. O. Harvey in the Geological Survey laboratories (1948) and is given opposite.

Calculation of the mineral content of the rock from the analysis shows that 83·6 % of the nodule consists of carbonate of the composition indicated. No calcite or dolomite was recognized in the rock and the carbonate appears to be wholly chalybite with values of ω ranging from

1·792 to 1·832. As compared with the carbonate of a similar rock-type (chalybite mudstone) from the Northampton Sand Ironstone[1] it is richer in $MgCO_3$ and $MnCO_3$ and poorer in $CaCO_3$: the content of $FeCO_3$ and the values of ω in the two cases do not differ greatly.

TABLE I. Analysis of iron carbonate nodule from Middle Lias.

Analyst, C. O. Harvey, Geological Survey Lab. no. 1518, Microsection no. E. 22355.

SiO_2	4·72
Al_2O_3	2·45
Fe_2O_3	1·64
FeO	41·68
MgO	4·34
CaO	6·13
Na_2O	0·22
K_2O	0·27
$H_2O > 105°$ C.	2·11
$H_2O < 105°$ C.	0·38
TiO_2	0·10
P_2O_5	1·77
MnO	0·60
CO_2	33·37
SO_3	0·07
Cl	trace
F	0·03
S	0·35
Cr_2O_3	nil
Li_2O	nil
BaO*	0·01
SrO*	0·05
	100·29
O for S and F	0·14
	100·15

Calculated mineral composition.

Collophane	$Ca_3(PO_4)_2$	3·9	
Gypsum	$CaSO_4.2H_2O$	0·1	
Pyrite	FeS_2	0·7	
Carbonates	$FeCO_3$	66·6	83·6
	$MgCO_3$	9·1	
	$CaCO_3$	7·0	
	$MnCO_3$	0·9	
Quartz	SiO_2	1·3	
Goethite	$Fe_2O_3.H_2O$	1·8	
Rutile	TiO_2	0·1	
Clay residue†		8·5	
		100·0	

† Including little white mica and felspar.

Composition of carbonate.

$FeCO_3$	79·7
$MgCO_3$	10·8
$CaCO_3$	8·4
$MnCO_3$	1·1
	100·0

Range of ω 1·792–1·832.

*Semi-quantitative spectrographic determinations by Dr. J. A. C. McClelland.

The figure of 1·3 % of quartz in the Middle Lias nodule is based upon a grain count. After satisfying the P_2O_5, SO_3, S, Fe_2O_3, and TiO_2 to give collophane, gypsum, pyrite, goethite, and rutile respectively, a residue of 8·5 % is left representing clay together with small amounts of white mica and felspar. While no very accurate significance can be attached to the percentages of the remaining oxides in this residue, the occurrence of appreciable amounts of Na_2O and K_2O may be indicative of the presence of an alkali clay, possibly corresponding to the mica-type mineral suggested by X-ray examination.

[1] J. H. Taylor, Petrology of the Northampton Sand Ironstone formation. Mem. Geol. Surv., 1949, pp. 48–50.

Minerals in the septarian cracks.

The septarian cracks range up to 15 mm. across, but the majority are less than 6 mm. wide. They are infilled, partially or completely, by one or more of the minerals calcite, baryte, pyrite, and zinc-blende. No trace of the 'specular-iron' recorded by Judd (loc. cit., p. 69) has been noted. Not infrequently successive deposition of material lining the walls of the fissure has given a banded structure to the resulting veinlet.

The commonest mineral of the septarian cracks is calcite. Many are occupied solely by this material, or by it in association with pyrite. In some cases the result is a veinlet in which finely disseminated pyrite is scattered irregularly through calcite (22356).[1] More commonly the veinlet is margined by pyrite and filled centrally by platy calcite (22357, 22362 C, 22363, pl. 1, fig. 1). The pyrite margins, which range in width from 0·05 to 0·4 mm., often show good crystalline form with crystals projecting into the central calcite. Locally the margins join and for a short distance the veinlet may consist wholly of pyrite. Commonly the wall-rock on either side of the fissure is stained brown for a distance of up to 0·4 mm. away from the pyrite. The continuity of the pyrite margins to the main fissure is here and there broken by small veinlets of calcite cutting across them (22362 B, 22363, pl. 1, fig. 1). No trace of marcasite is visible in polished section.

Another type of infilling consists wholly of calcite much of which has a spherulitic habit (22360–1). This consists of sheaf-like aggregates radiating from the walls of the fissure towards its centre and occupying in some cases a zone up to 3 mm. wide on either side of the veinlet. The central portion is commonly filled with clear platy calcite (pl. 1, fig. 2). In some cases this central zone is absent and the two sets of radiating sheaves meet along the median line of the veinlet. In another type of infilling calcite has a prominent bladed habit developed roughly parallel to the walls of the fissure (22362 C, 22466).

Baryte[2] as an infilling to the septarian cracks, though less abundant than calcite, is widespread. Commonly it develops the typical bladed or radiating habit: occasionally it projects as euhedral crystals into cracks only partially filled. None of these varieties exhibits any trace of fluorescence. A section of a typical baryte-filled veinlet (22464, pl. 1, fig. 3) shows tabular crystals projecting across the vein at right angles

[1] These numbers refer in all cases to the Geological Survey's English series of microscope slides.

[2] Spectrographic analysis by Dr. J. A. C. McClelland shows a strontium content in the baryte of approximately 2·5 %.

or obliquely. In other parts of the same septarian nodule the disposition of the laths is parallel to the walls of the fissure. In some cases (22464, 22466) single large baryte crystals occupy the full width of a veinlet. Marginal bands of pyrite are as common in the case of the baryte-filled cracks (22362, 22362 B, 22362 C) as with the calcite-filled ones.

Many septarian cracks contain both calcite and baryte. Commonly the junction between the two minerals is a sharp crystal boundary (22362 C, 22466, pl. 1, fig. 4), so that a vein filled with calcite passes suddenly into one filled with baryte. In other cases (22362 B, 22362 C) a thin impersistent zone of calcite 0·01–0·05 mm. across separates marginal pyrite from central baryte. Locally the calcite cuts through the pyrite and extends into the wall-rock (pl. 1, figs. 5–6). Occasionally the calcite zones on the two sides are linked by thin stringers (0·03–0·04 mm. wide) extending completely across the baryte. In 22466 calcite has infiltrated along cleavages of baryte and along junctions between individual crystals of baryte. Such examples provide clear evidence of replacement of baryte by calcite. The radiating or bladed habit exhibited by calcite in certain specimens (22360–1, 22362 C) is reminiscent of baryte, but there is no evidence to show that, in these cases, the calcite is, in fact, pseudomorphous after baryte.

Blende is also commonly present in the septarian cracks though in smaller quantity than calcite, baryte, or pyrite. Frequently it occurs as small triangular crystals or in aggregates of crystals growing like the teeth of a saw on one side of a common base line. These bodies are enclosed either in calcite (22358, 22364, 22465, 22467) or in baryte (22362 B, 22464). In one case (22362 B) some of the blende is clearly following cleavages in the baryte and locally blende is separated from baryte by a thin zone of calcite in exactly similar manner to that in which pyrite is separated from blende in the same specimen. No trace of blende following cleavages in the calcite was ever seen and it appears that none of the blende post-dates the calcite.

Origin of the septarian nodules and associated minerals.

The conformability of the bedding planes of the Lias to both upper and lower surfaces of the nodules, the flattened form of the nodules and their repeated arrangement in well-marked layers are suggestive of an origin subsequent to the deposition of the enclosing sediments.[1] They may well, however, have been formed at an early stage in the compaction

[1] W. A. Richardson, The relative age of concretions. Geol. Mag. London, 1921. vol. 58, pp. 114–124. [M.A. 1–399.]

of the Lias clays and silts by some form of colloidal segregation in the manner suggested for the clay-ironstone nodules from the Coal Measures by Tomkeieff (loc. cit.) and by North and Howarth.[1] Presumably the formation of calcite or chalybite in the nodules was controlled by the relative abundance of the hydrosols of Fe, Ca, and Mg at different horizons in the sediments. Gradual recrystallization of the nodules from outside with desiccation of the centre in the manner postulated by Richardson[2] would give rise to the system of septarian cracks.

The infilling of the septarian cracks was evidently a consequence of waters circulating through the nodules and depositing in cavities any substances present in a state of supersaturation. There seems little reason to doubt that these substances were derived from the surrounding sediments. The Middle Lias silts and silty clays are both calcareous and pyritic. Spectrographic examination of three samples from the *margaritatus* zone by Dr. J. A. C. McClelland have given the following semi-quantitive results:

Sample no.	Locality.	Percentages. Ba.	Zn.	Pb.
644	Ashwell railway cutting, 1150 yards NE. by N. of Westfield House, Rutland. Silty clay ...	0·02	0·05	0·03
673	Ashwell railway cutting, 1260 yards NNE. by N. of Westfield House, Rutland. Clay ...	0·02	trace	0·04
684	Bank of river Welland, 1200 yards NE. by N. of Rockingham church, Northants. Clay ...	0·02	trace	0·04

The figures for Ba are actually less than Goldschmidt's average for the earth's crust[3] of 390 gm. per ton (= 0·038 %) or Clarke's average for 78 shales[4] of 0·05 % BaO (= 0·045 % Ba). The Zn percentage of 0·05 from sample 644 (silty clay) is well above the figure of 40 gm. per ton (= 0·004 %) given by Goldschmidt for the average of the earth's crust,[3] and also that of 0·01 % for sedimentary rocks in general recently quoted by Guimarães.[5] Many sediments are, however, considerably richer in

[1] F. J. North and W. E. Howarth, On the occurrence of millerite and associated minerals in the Coal Measures of South Wales. Proc. S. Wales Inst. Eng., 1928, vol. 44, pp. 325–348. [M.A. **4**–84.]

[2] W. A. Richardson, On the origin of septarian structure. Min. Mag., 1919, vol. 18, pp. 327–338.

[3] V. M. Goldschmidt, The principles of distribution of chemical elements in minerals and rocks. Journ. Chem. Soc. London, 1937, pp. 655–673. [M.A. **7**–165.]

[4] F. W. Clarke, The data of geochemistry. 5th edit., Bull. U.S. Geol. Surv., 1924, no. 770, p. 30.

[5] D. Guimarães, Mineral deposits of magmatic origin. Econ. Geol., 1947, vol. 42, p. 733.

zinc than this figure indicates, as has been made clear by Goldschmidt.[1] The Pb percentages from the Middle Lias sediments (considerably in excess of Guimarães's average for sediments of 0·0016 %) are of interest in view of the fact that no trace of galena has been found in any of the nodules examined.

From the observed relations of the minerals in the septarian cracks it is evident that pyrite, which so commonly lines the walls of the fissures, was the earliest to be formed. It seems probable that there was considerable overlap in the periods of deposition of the other constituents. In some specimens blende is enveloped by and appears to have preceded baryte; elsewhere it follows cleavages in this mineral and is clearly later. Calcite also has in some cases infiltrated along cleavages in the earlier formed baryte; in others where calcite and baryte meet in sharp crystal boundaries they appear to be broadly contemporaneous. While there is locally evidence that calcite is later than the other three constituents of the vein there is nowhere any trace of these other minerals postdating a part of the calcite. The paragenesis of the four constituents of the septarian cracks can therefore be represented diagrammatically as follows:

Explanation of Plate I.

Photomicrographs of infillings of septarian cracks in Middle Lias nodules from Leicestershire and Rutland. (E numbers refer to microscope slides and M numbers to photographs in the Geological Survey collection.)

Fig. 1. Calcite mudstone nodule, bank of brook 850 yards W. by S. of church at Great Easton, Leicestershire. (E. 22363, M. 2316.) Septarian crack margined by pyrite and infilled centrally with platy calcite which at one point cuts across marginal pyrite. Crossed nicols. ×19.

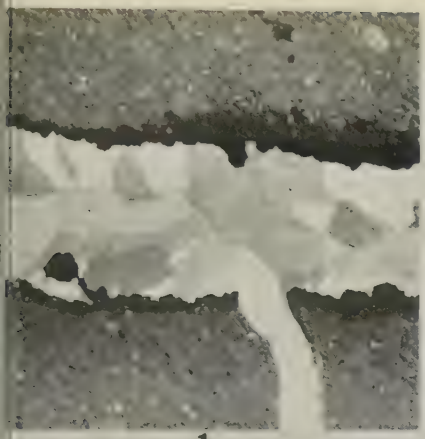
Fig. 2. Calcite mudstone nodule, bank of river Gwash 860 yards ESE. of church at Braunston, Rutland. (E. 22361, M. 2320.) Septarian crack infilled with marginal radiating calcite and central platy calcite. Crossed nicols. ×7.

Fig. 3. Chalybite mudstone nodule, bank of brook 1150 yards ESE. of railway station at Whissendine, Rutland. (E. 22464, M. 2317.) Septarian crack infilled with tabular baryte. Crossed nicols. ×16.

[1] V. M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente. IX. Die Mengenverhältnisse der Elemente und der Atom-Arten. Skrifter Norske Videnskaps-Akad. Oslo, I. Mat.-Naturv. Kl., 1938, for 1937, no. 4, pp. 81–82. [M.A. 7–166.]

FIG. 4. Calcite mudstone nodule, bank of river Gwash 770 yards ESE. of church at Braunston, Rutland. (E. 22362 C, M. 2314.) Junction of two septarian cracks margined by pyrite and infilled centrally by calcite (on left) and baryte (on right). Crossed nicols. ×19.

FIGS. 5–6. Calcite mudstone nodule, bank of river Gwash 770 yards ESE. of church at Braunston, Rutland. (E. 22362 B, M. 2321–2.) Septarian cracks margined by pyrite and infilled centrally with baryte (dark): calcite (pale) replacing baryte and locally cutting through marginal pyrite. Crossed nicols. ×33.



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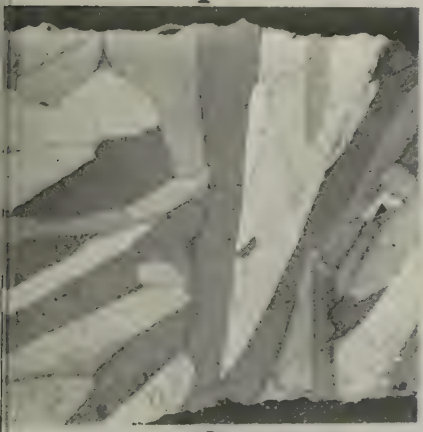

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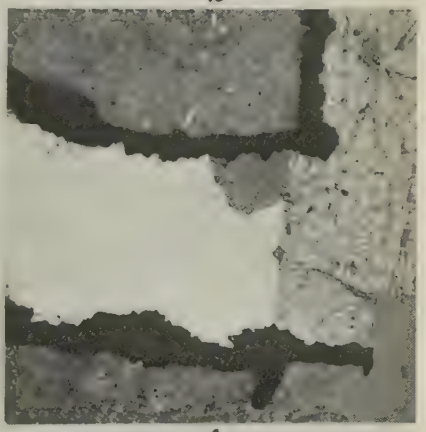

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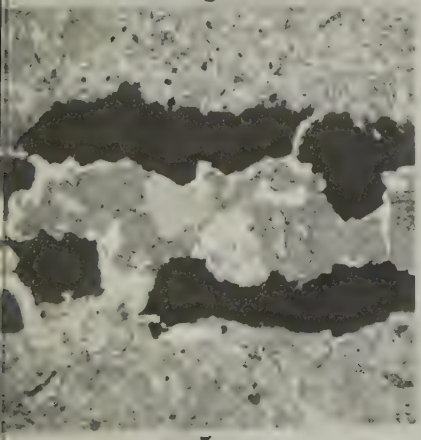

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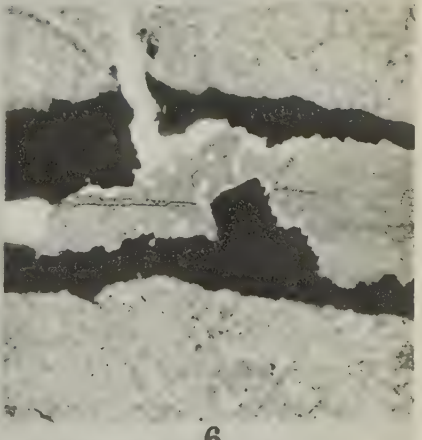

6

J. H. Taylor: Baryte, etc., in septarian nodules from the Lias

On the occurrence of neptunite and eudialyte in quartz-bearing syenites from Barnavave, Carlingford, Ireland.

By S. R. Nockolds, Ph.D., F.G.S.

Department of Mineralogy and Petrology, University of Cambridge.

[Read June 23, 1949.]

SOME years ago the author gave a short description of a quartz-bearing syenite and its xenoliths occurring on the eastern side of Barnavave.[1] The locality was revisited recently and more material was collected, while another outcrop of syenite was discovered[2] farther to the north at locality 5.

The new material collected at the original locality is not very different from that previously described. The syenite occurs as veins in limestone and, whereas all the previously described material was quartz-bearing, some of the syenite in very narrow veins is virtually free from quartz. Again, certain specimens carry a fair amount of late-crystallizing wollastonite which may be replaced to a varying degree by pectolite. The limestone at the contacts of the veins and present as xenoliths in the syenite mostly shows the development of a garnet-wollastonite reaction border, as detailed previously. But some of the smaller xenoliths are composed entirely of garnet and wollastonite or, more rarely, of the latter mineral alone. Moreover, in a number of specimens, pectolite becomes a noticeable constituent, forming largely at the expense of wollastonite, while aegirine-augite may also form from wollastonite in the outer zone in some cases.

The main point of interest in the new material is the presence here and there of the rare mineral *neptunite* in the syenite, a mineral previously unknown in the British Isles. It occurs sporadically, and never abundantly, as small interstitial flakes or partially replacing sphene and it formed at a late stage (fig. 1). It shows the characteristic striking pleochroism of neptunite with α pale yellow, β yellow-brown, γ orange-red, $\gamma > \beta > \alpha$, and has α 1·691, β 1·700, γ 1·735 (all $\pm$0·003) with (+) 2V about 40°; strong dispersion. The extinction is inclined and the angle between the two cleavages, measured in a section perpendi-

[1] S. R. Nockolds, Geol. Mag., 1937, vol. 74, p. 125.

[2] S. R. Nockolds, Min. Mag., 1947, vol. 28, map p. 156.

cular to both, is approximately 80°. These properties agree closely with those given by Larsen for Californian material.[1]

The syenite found farther to the north is also confined to veins in the limestone, which has been altered here to a fine-grained diopside-wollastonite-felspar-rock with accessory pale biotite, sphene, and iron ore, and with narrow bands and streaks of wollastonite-garnet-rock.

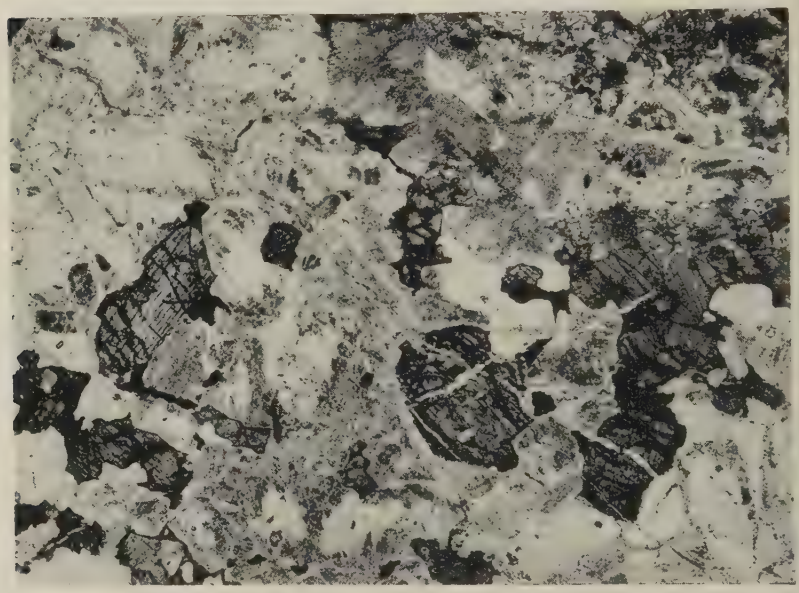

Fig. 1. Neptunite in quartz-bearing syenite, Carlingford. Ordinary light, × 20. The figure shows light potash-felspar and dark aegirine-augite and sphene. The deep-red neptunite appears black and occurs as little interstitial patches and veining sphene.

The syenite is again a quartz-bearing variety, but is virtually hololeucocratic, consisting simply of feebly microperthitic potash-felspar and interstitial quartz. The former must be close in composition to the normative felspar of the analysed rock which is $Or_{82}Ab_{16}An_2$. Here and there a small crystal of aegirine-augite occurs and sphene is the only noticeable accessory constituent, although a small quantity of neptunite was seen in one or two specimens.

Some of the veins carry a little wollastonite, often interstitial with respect to the felspar, and this is especially the case near their margins and in the narrower veins. This wollastonite has β 1·635 (±0·003) and

[1] E. S. Larsen, Bull. U.S. Geol. Survey, 1934, no. 848, p. 127. [M.A. 5–481.]

is frequently replaced by pectolite. The syenite in a number of the narrower veins loses most or all of its quartz, and may carry rather more aegirine-augite. A chemical analysis of a typical specimen, kindly made by Mr. H. C. G. Vincent, gave the following result:

			Norm.
SiO_2	68·50		
TiO_2	0·09		
ZrO_2	trace	qz	11·3
Al_2O_3	16·73	or	71·7
Cr_2O_3	nil	ab	14·1
Fe_2O_3	0·05	an	1·7
FeO	0·26	$MgSiO_3$	0·4
MnO	nil	$FeSiO_3$	0·3
MgO	0·17	mt	0·1
CaO	0·37	il	0·1
BaO	nil	ap	trace
Na_2O	1·67		
K_2O	12·12		99·7
H_2O+	0·13		
H_2O-	0·09	Sp. gr.	2·65
P_2O_5	0·04		
	100·22		

The rock is white in hand-specimen but occasionally small specks may be observed ranging in colour from pale pink to deep rose. There are also small segregation areas to be found, mostly in the neighbourhood of the limestone, which are composed essentially of quartz, aegirine-augite, and sphene, and these have frequently a pronounced pink flush pervading them. Examination of thin sections shows that this pink colour in the segregations and in the specks in the normal syenite is due to the presence of small crystals of *eudialyte* (fig. 2).

The little crystals are colourless in thin section with tabular habit, thus giving sections with negative elongation so that, at first sight, they closely resemble apatite. The curiously mottled appearance of the interference colours between crossed nicols, so characteristic of eudialyte, immediately distinguishes them. They are optically positive with ω 1·609, ϵ 1·614 (both $\pm$0·003). In grains the mineral is dichroic with ω pale pink, ϵ paler pink or colourless, $\omega > \epsilon$. To make quite sure that the mineral was eudialyte an X-ray powder photograph was kindly taken by Mr. K. Rickson and the lines compared with those of eudialyte from the Khibina complex in the Kola peninsula.

The interest of the occurrence is not only that it represents a mineral previously unknown in the British Isles, but that it is here occurring in intimate association with quartz. The only other record of eudialyte

associated with quartz known to the author is that described by Lacroix from Madagascar,[1] but this Madagascan eudialyte is rich in cerium earths and has higher refractive indexes than usual.

In his original paper on quartz-bearing syenite from the Carlingford area the author concluded that the syenite was a partial differentiate

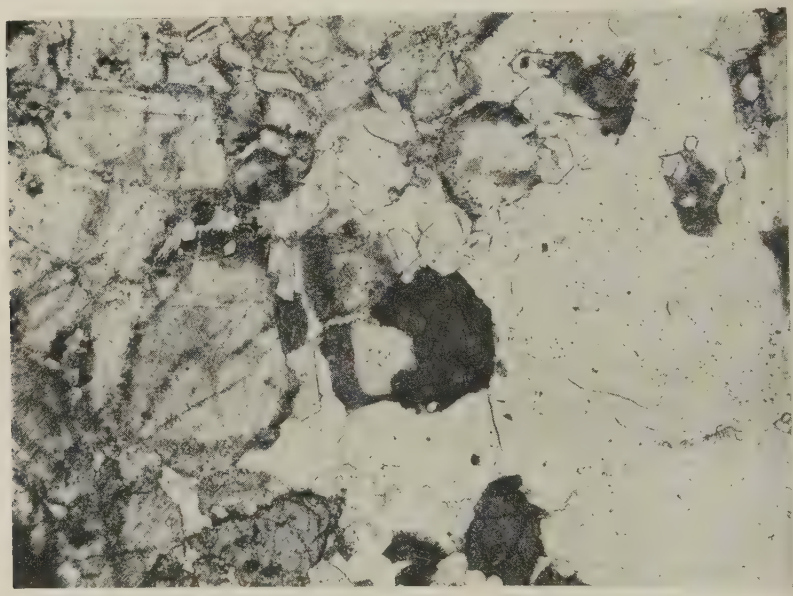

Fig. 2. Eudialyte, small segregation in hololeucocratic quartz-bearing syenite, Carlingford. Ordinary light, × 20.

On the left the figure shows the normal syenite with turbid potash-felspar and some quartz. The remainder of the figure represents a portion of a segregation consisting of quartz with aegirine-augite and sphene, together with small, colourless, crystals of eudialyte frequently hexagonal in form.

of the main granophyric granite, but further work has caused him to modify this view. Exposures are unfortunately poor in the area concerned, but it seemed clear after careful scrutiny in the field that the syenites occur only as veins in the limestone and are never found elsewhere. This suggests that the formation of the syenite is connected with the presence of limestone and that granite magma has been desilicated in some way to produce syenite, a suggestion strengthened by the fact that some of the very narrow veins of syenite lose all their quartz.

Knowing the composition of the granite of the district and of the

[1] A. Lacroix, Min. de Madagascar, 1922, vol. 1, p. 589.

syenites (see below), it is possible to find out what must be removed from the granite magma, assuming this has the same composition as the solidified granite, in order to produce the syenites.

	I.	II.	III.
SiO_2 ...	74·80	62·90	68·50
TiO_2 ...	0·23	0·56	0·09
Al_2O_3 ...	12·30	15·62	16·73
Fe_2O_3 ...	1·06	0·94	0·05
FeO ...	1·46	2·50	0·26
MnO ...	trace	0·03	nil
MgO ...	0·06	0·53	0·17
CaO ...	0·66	3·08	0·37
Na_2O ...	3·73	4·17	1·67
K_2O ...	5·29	8·65	12·12
H_2O+ ...	0·32	0·25	0·13
H_2O- ...	0·21	0·25	0·09
P_2O_5 ...	0·03	0·08	0·04
	100·15	99·56	100·22

I. Granite; average of two analyses. (Nockolds, Geol. Mag., 1935, vol. 72, p. 304, VII and VIII.)
II. Quartz-bearing syenite. (Nockolds, Geol. Mag., 1937, vol. 74, p. 126.)
III. Hololeucocratic quartz-bearing syenite (p. 29).

In the case of the normal quartz-bearing syenite, there is evidence that a small amount of calcium has been added to the magma from the xenoliths and limestone contacts.[1] Allowing for this, and assuming no loss of potassium, we find that the material which must be subtracted from the granite magma to produce the syenite has the following composition, so far as the major constituents are concerned: SiO_2 88·7, Al_2O_3 7·5, FeO 1·1, Na_2O 2·7. It can hardly be coincidence that these are the very constituents which were added to the limestone during its alteration. The reaction rim of the xenolith analysed in the earlier paper[2] showed a gain of much SiO_2, together with some Al_2O_3 and a little iron, and numerous other examples show the same kind of alteration. Then there are the examples carrying pectolite forming at the expense of wollastonite, and others with aegirine-augite, thus indicating a transport of sodium at a slightly later stage than the other constituents.

The hololeucocratic quartz-syenite has received no addition of calcium and, again assuming no loss of potassium, material of the following composition must be removed from the granite magma in order to produce the syenite: SiO_2 81·3, Al_2O_3 9·2, FeO 4·3, Na_2O 5·3. Here, however, the conditions were more complex because a partial analysis of the limestone at the contact, kindly made by Mr. J. H. Scoon, gave the following result: SiO_2 51·07, Al_2O_3 8·59, Fe_2O_3 (all Fe as Fe_2O_3) 2·73,

[1] S. R. Nockolds, Geol. Mag., 1937, vol. 74, p. 130.
[2] S. R. Nockolds, loc. cit.

Na_2O 2·70, K_2O 3·36. Thus potassium has been introduced as well as sodium, but the ratio of Na to K is higher than in the granite magma.

In the first case, the addition of calcium leads to the formation of pyroxene rather than plagioclase because of the concurrent removal of aluminium and, in both cases, this removal of aluminium leads to a small excess of sodium over aluminium in the remaining magma so that aegirine-augite was able to form. This relative richness in Na leads also to the formation of neptunite $[Na_2(Fe,Mn)(Si,Ti)_5O_{12}]$ and of eudialyte [essentially $(Na,Ca)_5(Zr,Fe)_2Si_6(O,OH,Cl)_{20}$] in place of sphene and zircon respectively.

When contamination occurs at contacts of granite magma with limestone, the former behaves in one of two ways. Either it becomes basified with formation of lime-bearing plagioclase and amphibole or pyroxene or, more rarely, it behaves as the Carlingford examples. This difference of behaviour is due, in the first instance, to the fact that, in the commoner case, calcium is added to the magma, but aluminium is not removed.

It seems to the author that this, in its turn, may possibly be explained by the kind of limestone at the contact. If the limestone is an impure one, already containing aluminous or siliceous impurity, the available calcium will combine with this during thermal metamorphism, with release of CO_2, before any contamination takes place. Therefore any reactions which go on during contamination take place between magma and silicate material. If, on the other hand, the limestone is relatively pure it will simply recrystallize largely as calcite and when this material comes into contact with the granite magma, silicon and aluminium can pass into the limestone combining with the calcium and releasing CO_2. Under these conditions, there may be little or no calcium available for reciprocal transfer to the magma and the reaction has the appearance of a more or less one-way transfer of material from the magma to the limestone.

Tilley has recorded recently from the island of Skye an occurrence of a marginal facies of peralkaline pyroxene-granite where a calc-alkali hornblende-biotite-granite comes up against Durness dolomites.[1] In this example, the dolomite has received silicon and aluminium from the granite magma, as has the limestone at Carlingford, but there is no evidence of selective transfer of soda. In spite of this, the modified granite is rich in potassium and in this respect is closely comparable with the hololeucocratic quartz-bearing syenite of locality 5 at Carling-

[1] C. E. Tilley, Geol. Mag., 1949, vol. 86, p. 81.

ford. It is evident that active transfer of sodium to the limestone is not a necessary accompaniment of potassium enrichment in the modified magma. In Skye the mass of granite magma has been relatively large so that the modified magma has not been appreciably desilicated. In the Carlingford example where the modified rock occurs as narrow veins in the limestone, desilication has occurred.

In conclusion, it should be noted that the type of desilication found at Carlingford is different from that envisaged by Daly in his well-known hypothesis about the production of alkali rocks from calc-alkali magmas by reaction with limestone,[1] and it may prove eventually to have some importance in connexion with the petrogenesis of certain alkaline rocks.

[1] R. A. Daly, Bull. Geol. Soc. America, 1910, vol. 21, p. 87; Journ. Geol. Chicago, 1918, vol. 26, p. 97.

On paratacamite and some related copper chlorides.[1]

By Clifford Frondel, Ph.D.

Harvard University, Cambridge, Massachusetts.

[Read by Dr. F. A. Bannister, November 10, 1949.]

Paratacamite.

In the course of a study of the corrosion products formed by sea-water sprayed at a temperature of 85° F. on brass and copper sheets, a pale green compound was isolated which proved on chemical analysis to have the composition $Cu_2(OH)_3Cl$. The X-ray powder diffraction pattern of the substance was found on visual comparison to differ from that of atacamite, which has the same chemical composition. The atacamite pattern was obtained from a specimen of the mineral from Moonta, on the Yorke peninsula, South Australia, that had been authenticated by both morphological measurement and optical study; identical patterns were obtained from a number of other specimens labelled atacamite. The pattern of the corrosion product proved to be identical, however, with that of two specimens in the Harvard collection labelled paratacamite. These were labelled as from Remolinos, Vallinar, Chile (no. 97523), and from Sierra Gorda, Chile (no. 82883).

Paratacamite was originally described by G. F. Herbert Smith[2] in 1906 as a rhombohedral species dimorphous with atacamite. The described material came from the Herminia and Generosa mines at Sierra Gorda, Chile, and another occurrence is mentioned at the Bolaco mine, San Cristobal, Chile. Paratacamite was later said by Ungemach[3] on the basis of certain geometrical relations to be only twinned atacamite, and this conclusion has been accepted in standard mineralogical reference works.

The Harvard specimen from Remolinos comprised a dense mass of antlerite in which were embedded greenish-black crystals of rhombohedral habit. The observed physical properties and the chemical composition as found by analysis corresponded to the original paratacamite of Smith. The crystals, which ranged up to 2 millimetres in size, were

[1] Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 308.

[2] G. F. H. Smith, Paratacamite, a new oxychloride of copper. Min. Mag., 1906, vol. 14, pp. 170–177.

[3] H. Ungemach, L'atacamite. Bull. Soc. Franç. Min., 1911, vol 34, pp. 148–216.

markedly composite with curved and irregular surfaces. Approximate morphological measurements by the reflecting goniometer identified the forms present as $c(0001)$, $r(10\bar{1}1)$, and $f(02\bar{2}1)$; an idealized drawing is given in fig. 1. The Sierra Gorda specimen comprised irregular masses of the mineral associated with caracolite and schwartzembergite.

Through the courtesy of Dr. F. A. Bannister, Deputy Keeper of Minerals in the British Museum, crystals of paratacamite from the type material (B.M. 86958) of Smith were offered for study. Another authentic specimen of paratacamite was obtained from the U.S. National Museum (no. 95146). The latter specimen bore the notation that it had been purchased in 1904 from Mr. F. H. Butler, from whom the British Museum obtained the specimens studied by Smith. The X-ray powder patterns of the above-mentioned specimens of paratacamite proved to be identical with those of the Harvard specimens and of the corrosion product first mentioned.[4] A comparison of the chemical analyses, optical properties, and specific gravity of the Remolinos and type Sierra Gorda material is given in table I. The thermal curves for paratacamite and

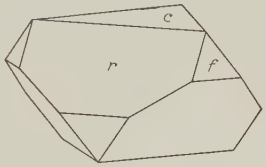

FIG. 1. Crystal habit of paratacamite from Remolinos, Chile. Forms $c(0001)$, $r(10\bar{1}1)$, $f(02\bar{2}1)$.

TABLE I. Chemical analyses of paratacamite.

	1.	2.	3.
Cu	14·27	14·60	14·88
CuO	56·10	55·98	55·87
Cl	15·97	16·29	16·60
H_2O+ ...	14·10	13·10	12·65
H_2O- ...	—	0·03	—
	100·44	100·00	100·00
Sp. gr.	3·74	3·72	—
ω	1·842	1·843	—
ϵ	1·848	1·849	—

1. Paratacamite. Generosa mine, Sierra Gorda, Chile. Analyst, G. T. Prior (Smith, 1906).

2. Paratacamite. Remolinos, Chile. Analyst, L. C. Peck, 1948. Analysis recalculated to 100 after deducting 0·97 % insoluble.

3. $Cu_2(OH)_3Cl$. Theoretical composition of paratacamite and atacamite.

[4] The non-identity of paratacamite and atacamite was established independently by X-ray study by F. A. Bannister in an unpublished study made while this work was in progress.

atacamite as obtained by the differential thermocouple method are shown in fig. 2.

Optically, both the Remolinos material and the type Sierra Gorda crystals were uniaxial positive without perceptible dichroism. Many grains were biaxial, apparently due to strain, with 2V ranging up to about 50° and with strong dispersion of the optic axes, r > v. The indices of refraction, measured by the immersion method in phosphorus–

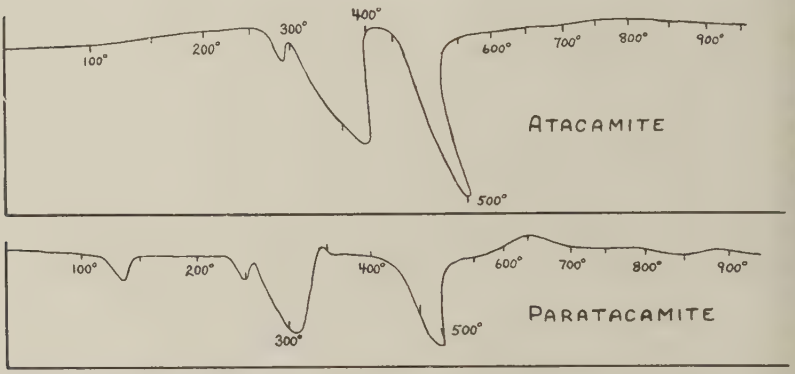

FIG. 2. Tracings of thermal curves of atacamite and paratacamite obtained by the differential thermocouple method using an Esterline–Angus graphical recorder.

methylene iodide liquids, were ω 1·843, ϵ 1·849 (Remolinos), and ω 1·842, ϵ 1·848 (Sierra Gorda), all $\pm$0·003. The extinction often was undulant or patchy, and the ultra-blue was shown in most orientations. Closely spaced polysynthetic twinning lamellae were present locally in crystals from both localities. The mean (?) index of refraction of a Sierra Gorda crystal was determined by Smith by the prism method as 1·846 (Na).

An X-ray study by the Weissenberg method was made of a single-crystal from the British Museum type specimen from the Generosa mine. All of the available crystals were complexly twinned, as described by Smith;[5] the crystal selected was a cuboid rhombohedron (10$\bar{1}$1) that contained several narrow twin lamellae on one side. These lamellae were avoided by suitably positioning the crystal in the X-ray beam, but it is not known if microscopic polysynthetic twin lamellae were also present, due to the opacity under the microscope of the relatively large-sized crystal required. The lattice-type proved to be rhombohedral.

[5] In fig. 1 of Smith's paper, showing a twin on (10$\bar{1}$1), the form letters *a* and *e* should be transposed.

The unit-cell dimensions are a 13·65 and c 13·95 kX in hexagonal co-ordinates, with $a:c$ = 1:1·022. This cell is identical with the morphological unit of Smith, who obtained $a:c$ = 1:1·0248. The ideal cell contents in the hexagonal unit are $Cu_{48}(OH)_{72}Cl_{24}$. The calculated specific gravity, 3·75, agrees satisfactorily with the value 3·74 directly measured by Smith on the same material. The cell dimensions in rhombohedral co-ordinates are a_{rh} 9·150 kX, α 96° 28′, and the corresponding cell contents are $Cu_{16}(OH)_{24}Cl_8$. There is a very strongly marked pseudo-cell with a halved in the hexagonal unit. These findings conclusively re-establish the species validity of paratacamite. The dimorphous substance atacamite is orthorhombic, with a 6·01, b 9·13, c 6·84 kX, and the space-group $Pnam$ according to Thoreau and Verhulst.[6] The two substances, however, are probably closely related structurally. This is indicated by a near identity in the position and relative intensity of the stronger lines in their X-ray powder patterns, and by the morphological similarities remarked by Ungemach and by Smith. The X-ray powder spacing data for artificial paratacamite is given by Rooksby and Chirnside.[7] An angle table for the known forms of paratacamite, all originally reported by Smith, is given in table II.

TABLE II. Angle table for paratacamite.

Hexagonal—R; hexagonal scalenohedral—$\bar{3}\ 2/m$

$a:c$ = 1:1·0248; x = 96° 23′; $p_0:r_0$ = 1·1833:1; λ = 82° 49½′

			ϕ	$\rho = C$	A_1	A_2
c	0001	111	—	0° 00′	90° 00′	90° 00′
a	$11\bar{2}0$	$10\bar{1}$	0° 00′	90 00	60 00	60 00
w	$20\bar{2}5$	311	30 00	25 19½	68 15	90 00
v	$7.0.\bar{7}.13$	922	30 00	32 30	62 16	90 00
u	$40\bar{4}7$	511	30 00	34 04	60 59	90 00
r	$10\bar{1}1$	100	30 00	49 48	48 35½	90 00
e	$01\bar{1}2$	110	−30 00	30 36½	90 00	63 50
f	$02\bar{2}1$	$11\bar{1}$	−30 00	67 05½	90 00	37 05
l	$24\bar{6}1$	$31\bar{3}$	−10 53½	80 55½	71 08½	49 43½

Synthetic paratacamite.—Paratacamite can be synthesized in several ways in addition to its formation by the action of salt-water spray on copper sheets. The substance is quickly formed when cuprous chloride

[6] J. Thoreau and J. Verhulst, L'atacamite du Katanga. Bull. Acad. Roy. Belg., 1938, ser. 5, vol. 24, pp. 716–720. See also H. Brasseur and J. Toussaint, Structure cristalline de l'atacamite. Bull. Soc. Roy. Sci. Liége, 1942, vol. 11, pp. 555–566. [M.A. 7–389, 9–225.]

[7] H. P. Rooksby and R. C. Chirnside, The formation of basic copper chloride and its identity with atacamite. Journ. Soc. Chem. Indust., 1934, vol. 53, pp. 33T–35T.

is exposed to a moist atmosphere or is strewn over wet filter-paper. The product gives a weak and diffuse X-ray pattern, due to a small particle size, and contains a considerable amount of non-essential water. The artificial products also usually contain more or less admixed malachite if precautions are not taken to exclude CO_2. Specimens of nantokite, CuCl, from Nantoko, Chile, and from Broken Hill, New South Wales, that had been exposed to the air for many years, were found to have completely altered to pulverulent masses of greyish-green paratacamite. Specimens of eriochalcite (antofagastite), $CuCl_2.2H_2O$, from Quetena mine, Chile, also were found to have altered in part to paratacamite. Another verified synthesis, originally described by Berzelius, consists of placing crinkled sheets of copper over filter-paper moistened with extremely dilute HCl. Rooksby and Chirnside[7] have earlier noted the formation of paratacamite by the corrosion of copper wire in seawater and in solutions of various chlorides; they refer to the substance as atacamite, but their X-ray powder spacing data are identical with those of paratacamite. Compounds with the composition $Cu_2(OH)_3Cl$ but not otherwise identified have been synthesized more recently by several workers.[8]

Through the interest of Mr. R. J. Gettens of the Fogg Art Museum, Harvard University, an opportunity was had to examine the green patina and alteration crusts present on various ancient copper and bronze objects. The detailed mineralogy of the alteration products need not be described here, but both paratacamite and atacamite were identified in numerous instances. Atacamite has been earlier described from such occurrences, but paratacamite appears to be much the more common of the two substances. Crystals of atacamite up to 0·5 mm. in size were found associated with malachite, chessylite, and cassiterite on an Egyptian bronze bull of the XIXth Dynasty. Paratacamite has so far been found only as dense to pulverulent coatings and not as distinct crystals. Mr. Gettens states that instances have been observed in which freshly cleaned, acid-washed cupreous objects have become thickly coated with a flocculent green coating in the course of a few days. One such coating here examined proved to be paratacamite.

[8] H. Martin, R. L. Wain, and E. H. Wilkinson, Studies upon the copper fungicides. Ann. Applied Biology, Cambridge, 1942, vol. 29, pp. 412–438. E. Montignie, Action de l'oxyde cuivreux sur divers composés. Bull. Soc. Chim. Paris, 1940, ser. 5, vol. 7, pp. 229–231.

Atelite.

Atelite, described by A. Scacchi[9] in 1873, was found on Vesuvius in fumaroles of the eruption of April, 1872. The substance occurred as more or less complete pseudomorphs after tenorite and was formed by the action on this mineral of hydrochloric acid fumes. An analysis gave CuO 45·59, $CuCl_2$ 38·9, H_2O and loss [16·22], total [100·00]. This analysis corresponds to $Cu_3(OH)_4Cl_2.H_2O$. Zambonini[10] found the atelite pseudomorphs to be isotropic.

Three specimens labelled atelite were available in the Harvard collection. One of these (no. 82886) comprised a small piece of scoriaceous lava locally encrusted by green, rather pulverulent pseudomorphous crystals with an acicular or lath-like habit. Some of the crystals had a corroded core of tenorite and unaltered tenorite was present on other parts of the specimen. The X-ray powder pattern of the green mineral checked that of paratacamite exactly. Under the microscope the substance appeared to be isotropic and had a variable and relatively low mean index of refraction ranging from about 1·82 to 1·84. These differences in optical behaviour from ordinary paratacamite are attributed to aggregate polarization in a minutely crystalline mass containing non-essential water. Interior parts of the pseudomorphs immediately adjacent to the tenorite cores had a relatively deep green colour and had the highest values for the mean index of refraction. The loose label on the specimen carries the notation 'Atelite. Vesuvius', and the Museum records show only that the specimen was purchased in 1911 from the now deceased mineral dealer Mr. Lazard Cahn.

Another specimen labelled 'Atelite. Vesuvius. Eruption of 1872' (no. 90168) comprised two sealed glass tubes containing a green substance which proved to be powdered malachite. This specimen obviously is fictitious. The third available specimen (no. 82885) comprised a sealed glass tube containing a green powder. This material gave the X-ray powder pattern of paratacamite plus a number of faint extra lines due to admixture. Optically, the bulk of the sample was composed of fine granular masses and flakes of a grass-green mineral with very low birefringence which showed the ultra-blue at extinction. The mean index of refraction, somewhat variable, was mostly about 1·805 with some

[9] A Scacchi, Contribuzioni mineralogiche . . . dell'incendio vesuviano . . . di aprile 1872. Rend. Accad. Sci. Fis. Mat. Napoli, 1873, vol. 12, pp. 165–168; Atti, 1875, vol. 6, no. 9, pp. 1–69. (Atelite, p. 22.)

[10] F. Zambonini, Mineralogia Vesuviana. 2nd edition, Napoli, 1935, p. 90 (eriochalcite), p. 111 (melanothallite), p. 112 (hydromelanothallite), p. 113 (atelite),

grains over 1·81. Many grains appeared to be single-crystal fragments, but these too had a birefringence and indices of refraction under those of ordinary paratacamite. The cause of this divergence is not known. The sample contained about 20 % of an unidentified green acicular mineral which penetrated the paratacamite and which appeared to be an alteration product thereof. Scattered grains of several other unidentified minerals were also present. It may be concluded that atelite of Scacchi is identical with paratacamite. Particular weight must be attached to the first specimen mentioned above. While this specimen cannot be shown to be type material, it does answer the original description in every detail. Although atelite as an incompletely (ἀτελής) described mineral has priority, it is proposed to retain the more appropriate name paratacamite for the species.

Tallingite.

Tallingite, named after R. Talling of Lostwithiel, who collected the first specimens, was described by A. H. Church[11] in 1865 as a new hydrated cupric oxychloride. The mineral was found at the Botallack mine, St. Just, Cornwall, as blue inclining to green (turquoise-blue) minutely globular or small-botryoidal crusts. The hardness was given as 3 and the specific gravity as about 3·5. An analysis of material dried over H_2SO_4 in vacuo gave CuO 66·24, Cl 11·33, H_2O [24·99], total less O for Cl [100·00], from which was derived the formula $Cu_5(OH)_8Cl_2.4H_2O$.

A specimen labelled tallingite from the Botallack mine, Cornwall, was available in the Harvard collection. This specimen (no. 82884) was originally from the collection of A. F. Holden and its prior history is not known. The specimen corresponds in every peculiarity to the characters of the original material as described by Church and is deemed to be authentic. The greenish parts of the crusts, in part smooth and enamel-like but mostly minutely globular and dull in lustre, were found by optical and X-ray study to be paratacamite. Optically, the mineral appears as fine-fibrous spherulitic growths or matted aggregates. The individual crystals are too small to permit precise optical measurements; the mean index of refraction is about 1·840 and individual fibres show the ultra-blue at extinction. The bluish parts of the crusts contain admixed particles of a blue mineral, which appears elsewhere on the specimen as relatively pure botryoidal crusts. This mineral could not

[11] A. H. Church, On some hydrated cupric oxychlorides from Cornwall. Journ. Chem. Soc. London, 1865, vol. 18 (n. ser., vol. 3), pp. 77–83. Here the description and analysis of a new mineral: the name tallingite first appeared in a later part (pp. 213, 214) of the same volume.

be identified. Since Church spoke of tallingite as being both green and blue he may have analysed a mixture.

Another specimen of tallingite was obtained for study from the British Museum (no. 36536). This specimen was bought of R. Talling in 1865, at the same time that Talling supplied material to Church, and was originally registered as atacamite and subsequently relabelled as tallingite. This specimen closely resembles that described from the Harvard collection, and was found to be a gross mixture containing paratacamite.

These observations taken alone would suggest the identity of tallingite with paratacamite. However, Dr. F. A. Bannister from a more detailed examination of other specimens concludes that tallingite is in reality an independent species. His results will be published later.

Botallackite.

Botallackite was originally found associated with atacamite and tallingite at the Botallack mine, Cornwall, and was described by A. H. Church[12] in 1865. His analysis gave CuO 66·25, Cl 14·51, H_2O 22·60, total 103·36, which indicates the formula $Cu_4(OH)_6Cl_2.3H_2O$. The mineral was said to form pale mountain-green crusts composed of minute interlacing crystals. The specific gravity was given as about 3·6.

A specimen of botallackite was obtained for study from the British Museum (no. 36528). This specimen had been originally obtained from Mr. Talling, who at the same time supplied specimens of the same mineral to Church, and hence can be presumed to be authentic. The physical characters of the material at hand answer the original description. The optical properties and the X-ray powder pattern of the mineral differ entirely from those of paratacamite and also from those of other known copper minerals as far as could be determined. The X-ray powder spacing data are given in table III. Optically, botallackite is biaxial positive with a moderately large 2V and strong dispersion, r > v. The indices of refraction are α 1·775 ± 0·003, β 1·800 ± 0·005, γ 1·846 ± 0·003. There is a good cleavage perpendicular to γ, and the mineral is weakly pleochroic in shades of bluish-green. Sufficient material was not at hand for a complete re-examination of this species. Qualitative tests and a spectrographic examination indicated the presence of only Cu, Cl, and H_2O as major constituents. Botallackite has been made identical with atacamite in both Dana's 'System of mineralogy', 6th edition, and Hintze's 'Handbuch der Mineralogie', but the

[12] A. H. Church, Notes on a Cornish mineral of the atacamite group. Journ. Chem. Soc. London, 1865, vol. 18 (n. ser., vol. 3), pp. 212–214.

present observations indicate that it is a distinct species. This same mineral has been identified by X-ray study as constituting a powdery greenish-blue incrustation on an Egyptian bronze Bast (goddess) in the

TABLE III. X-ray powder spacing data for botallackite. Copper radiation (λ 1·9418 Å.), nickel filter.

d.	*I.*	*d.*	*I.*	*d.*	*I.*
5·66	10	1·93	3	1·42	1
4·14	½	1·89	1	1·41	1
3·26	½	1·81	½	1·37	1
2·84	4	1·70	½	1·35	2
2·68	3	1·62	1	1·32	2
2·57	7	1·60	2	1·30	1
2·46	1	1·58	1	1·28	2
2·40	8	1·56	1	1·25	3
2·06	2	1·53	4	1·23	1
1·98	2	1·48	2		

collection of the Fogg Art Museum (no. 1943 1121B). The substance apparently is of recent origin. Another specimen supposedly of botallackite from the Botallack mine obtained from the U.S. National Museum (no. R1348) proved on examination to be brochanthite.

MELANOTHALLITE AND HYDROMELANOTHALLITE.

Melanothallite was described by A. Scacchi[13] in 1870 as black scales occurring with eriochalcite, hydrocyanite, euchlorine, and dolerophanite as a sublimation product in the crater of Vesuvius. The substance was said to change rapidly in colour from black to green on exposure, due to hydration, and to be soluble in water to a solution giving an acid reaction. An analysis by E. Scacchi[14] of the green alteration product afforded CuCl 57·37, CuO 31·39, H_2O [11·24], total [100·00]. This analysis corresponds to the formula $Cu_2(OH)_2Cl_2.H_2O$. The original melanothallite before hydration to the green phase was thought by E. Scacchi to have the composition Cu(OH)Cl. Zambonini considered the original substance to have been $CuCl_2$, and introduced the name hydromelanothallite for the green alteration product thereof examined by himself and earlier by E. Scacchi. Zambonini[10] also considered that a green mineral found in fumaroles on Vesuvius in 1906 and described by Lacroix[15] doubtfully as melanothallite to be identical with hydromelanothallite.

[13] A. Scacchi, Dell'eriocalco e del melanotallo, nuovo specie di minerali. Rend. Accad. Sci. Fis. Mat. Napoli, 1870, vol. 9, pp. 86–89.

[14] E. Scacchi, Sull'euchlorina, sull'eriocalco e sul melanotallo. Rend. Accad. Sci. Fis. Mat. Napoli, 1884, vol. 23, pp. 158–165. [Min. Mag. **12**–382.]

[15] A. Lacroix, Les minéraux des fumerolles de l'éruption du Vésuve en avril. 1906. Bull. Soc. Franç. Min., 1907, vol. 30, pp. 219 266. (Melanothallite ?, p. 224.)

Two specimens labelled hydromelanothallite from Vesuvius were available for examination. One of these, obtained from the British Museum (no. 46393), consisted of emerald-green granules without crystal form. Optically, this substance is biaxial positive with a moderately large 2V. The indices of refraction and the pleochroism are α 1·580 (pale grass-green), β 1·605 (grass-green), γ 1·644 (bright yellow-green), all $\pm$0·003. The mineral has at least two cleavage directions, one of which is perfect in quality and is perpendicular to α. A few elongated grains with a semblance of prismatic crystal outline, and other grains with an elongated shape due to cleavage, were found to give parallel extinction: hence the mineral is probably orthorhombic. A few grains of another mineral, probably dolerophanite, were found admixed in the sample. The indices of refraction are much too low for a mineral of the composition attributed to hydromelanothallite. Qualitative tests showed the presence of large amounts of sodium, potassium, and sulphate, in addition to copper, and the X-ray powder pattern proved to be identical with that of a specimen of uncertain authenticity in the Harvard collection labelled euchlorine from Vesuvius. Euchlorine is described as orthorhombic, with the supposed composition $(K,Na)_2SO_4.2CuSO_4.CuO$, but the species is not well defined.

The second specimen of reputed hydromelanothallite examined was from the collection of the U.S. National Museum (no. R1345). Under the microscope, this material appeared as fibrous masses or coarse needle-like crystals with parallel extinction. Satisfactory optical data could not be obtained because of a surface alteration of the crystals. The mineral in general resembles that of the British Museum specimen, but the green colour inclines more towards yellow and the indices of refraction are higher. The substance is biaxial positive, with $\alpha \sim 1{\cdot}591$ and $\gamma \sim 1{\cdot}707$. There is a good cleavage, and γ is parallel to the elongation. Qualitative tests proved the presence of copper, sulphate, chloride, and alkalis with relatively more K than Na. The X-ray powder pattern differed from that of the mineral above described and also from that of paratacamite and of other known copper minerals in so far as could be determined. This mineral might also be euchlorine, then leaving the identity of the British Museum and Harvard specimens unknown, but more likely is a hitherto unrecognized species. In any case, neither of the specimens represents hydromelanothallite and the species validity of this mineral remains uncertain.

Eriochalcite and Antofagastite.

The first accurate description of orthorhombic $CuCl_2.2H_2O$ as a mineral was made by Palache and Foshag[16] in 1939 on material from the Quetena mine, near Calama, Antofagasta province, Chile. Their mineral, to which the name antofagastite was given, corresponds exactly in all characters with the artificial compound. It occurs as lichen-like aggregates of crystals coating fracture surfaces of rock in the uppermost oxidized zone of the deposit and is immediately associated with atacamite and bandylite. An ill-defined but apparently similar mineral was described under the name eriochalcite in 1870 by A. Scacchi.[13] The latter mineral occurred as pale blue, wool-like incrustations associated with melanothallite in fumaroles of the eruption of 1869 of Vesuvius. Eriochalcite was originally described as a chloride of copper on the basis of qualitative tests. A later partial quantitative analysis by E. Scacchi[14] in 1884 of a water extract of the crusts gave the ratio Cu:Cl = 1:2 from the determined weight percentages, Cu 48·08 and Cl 51·92. In 1910, Zambonini[10] examined an apparently authentic sample that had been preserved by sealing in a glass tube. The water content was determined as 20·50 %, which in conjunction with the earlier partial analysis of E. Scacchi established the composition as $CuCl_2.2H_2O$. Zambonini, however, concluded from ambiguous optical evidence that the substance probably was monoclinic and dimorphous with the ordinary, orthorhombic form of $CuCl_2.2H_2O$. Lacroix[15] also expressed the view that the substance had the composition $CuCl_2.2H_2O$.

An authentic specimen of eriochalcite was obtained by the Harvard Museum in 1947 from the mineral dealer Mr. Roberto Palumbo of Rome. The pale-blue, wool-like sample (no. 97927) was sealed in a short glass tube and bore a glued-on label with the notation 'Vesuvio. 1869' in the handwriting of A. Scacchi as identified from other museum labels in the Harvard collection, together with another loose label identifying the specimen as eriochalcite from the collection of E. Scacchi. A letter from Mr. Palumbo states that the specimen was given to him by the son of E. Scacchi. A comparison by X-ray and optical methods of this material with type specimens of the antofagastite of Palache and Foshag and with artificial orthorhombic $CuCl_2.2H_2O$ has established the complete identity of the three substances. The name eriochalcite has priority and should be retained for the species. The name was originally written as eriocalco (from ἔριον, wool, and χαλκός, copper, in allusion

[16] C. Palache and W. F. Foshag, Antofagastite and bandylite, two new copper minerals from Chile. Amer. Min., 1938, vol. 23, pp. 85–90. [M.A. 7–59.]

to the form of aggregation) which properly transforms to eriochalcite rather than eriocalcite. The synonymous forms erythrocalcite and Erythrochalcit given by Dana[17] and by Groth,[18] respectively, are undesirable because they imply that the substance is red in colour, whereas the mineral actually is blue.

[17] E. S. Dana, System of mineralogy. 6th edition, New York, 1892, p. 174.

[18] P. Groth, Tabellarische Übersicht der Mineralien. 4th edition, Braunschweig, 1898, p. 52.

The chemical composition and physical properties of the residual glass of the Kap Daussy tholeiite dike, east Greenland.

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Introduction.

In the course of a petrological examination of some hundreds of specimens from the Tertiary coastal dike swarm of east Greenland, collected at various times by L. R. Wager and W. A. Deer, it was decided to investigate the nature of the residual glassy mesostasis of one of the olivine-tholeiites, in the hope that it might shed some light on the trend of differentiation of the magma responsible for the bulk of the rocks in the swarm. An account of the petrology of the swarm as a whole will be published in due course, but it was thought that a note on the chemical and physical properties of this glassy residuum might be worthy of independent publication, particularly as it provides an interesting comparison with the results of work carried out by Walker (1930, 1935) on the residual glass from one of the Upper Carboniferous tholeiites from central Scotland. The general features of the east Greenland coastal dike swarm have already been described by Wager and Deer (1938) and Wager (1947).

The Kap Daussy tholeiite.

The particular specimen investigated, which is here called the Kap Daussy tholeiite, was taken from a dike, 20 feet in width, about 300 yards east of the south-west point of Kap Daussy, south-west of Scoresby Sound, in latitude 68° 40′ N., longitude 26° 40′ W. Seven dikes were sampled between the south-west point of Kap Daussy and a point about one mile to the east. All these carry a certain amount of devitrified glass or late crystallized residuum, but the Kap Daussy dike dealt with here is the only one with an appreciable quantity of fresh glass. It cuts, and is chilled against a dike 12 feet wide which is the third dike east of the south-west point of Kap Daussy.

The dike rock itself is a fresh basic rock, with a little olivine and a light brown residual glass, patchy in its distribution and generally showing intersertal texture with respect to the other minerals (fig. 1). In texture, and in mineralogical and chemical composition, the rock closely resembles some of the tholeiites of the Salen type described (Bailey, 1924) from the Mull Tertiary swarm, and the chemical analysis of one of these latter is reproduced, for purposes of comparison, in table I (p. 56). The Kap Daussy rock will be called a tholeiite, cf. Salen type.

In table I are given also the chemical analyses of the Kap Daussy tholeiite (E.G. 1123) and the Kinkell (Dumbartonshire) tholeiite investigated by Walker (1935) together with norms and modes. It will be seen that the Kap Daussy and Mull tholeiites are, on the whole, very similar chemically. The Greenland rock is richer in iron oxides and rather poorer in alumina than the Mull rock, though the sum of these constituents is much the same in both. Titania is also a good deal higher in the Kap Daussy rock, but in all other respects there is close agreement. Physical and chemical data for the residuum of the Mull rock are not given in the Mull memoir, but the similarity in chemical composition with the Greenland rock makes it appear possible that the residua will also be somewhat similar.

The writer is indebted to Dr. K. C. Dunham for providing a chip of this analysed Salen tholeiite (Geol. Surv. S. 16808) from the Survey collection. In the crushed and separated material it is seen that the mesostasis is not a fresh glass as in the Kap Daussy rock, but is practically all altered to palagonitic material very similar to that which is present in small amount in the Kap Daussy rock. One or two fragments of unaltered glass from the Mull rock have a refractive index around 1·50, while the refractive index of the birefringent palagonitic material covers a range from about 1·55 to 1·60.

The analysis of the Kap Daussy rock deviates rather more widely from Walker's Kinkell tholeiite (analysis B) which is considerably richer in total alkalis and in potash and has rather less iron, lime, and magnesia. Titania is high, and alumina also is closer to the figure for the Kap Daussy rock than for the Mull example. Walker (1935) remarks that among the Carboniferous dolerite intrusions of central Scotland the alumina content tends to be rather lower in the tholeiitic rocks (mostly between 11·25 and 12·15 %) than in the associated quartz-dolerites (12·70 to 14·61 % in the examples there cited), and the alumina figure for the Greenland tholeiite under discussion is similarly

rather lower than for other dolerite dikes in the same swarm which have so far been analysed.

Consideration of the calculated norms and measured modes for the Kap Daussy and Kinkell tholeiites (table I) shows at once the acid

Fig. 1. Photomicrograph of the Kap Daussy, east Greenland, tholeiite showing an unusually large area of residual glassy mesostasis with inclusions. Ordinary light. ×45.

nature of the glassy mesostasis. In neither rock does quartz appear as a crystalline phase, yet silica in excess is present to a small extent in the norms of both: indeed, there is 7·6 % of normative quartz in the Kinkell rock, where the amount of residual glass is considerably more than in the Greenland one. The latter actually contains a little olivine (about 4 %), which appears in the norm as hypersthene (together with a little excess silica), because of the silica-rich glass.

The residual glass.

The glass (fig. 1) in the Kap Daussy tholeiite is rather patchily distributed, occurring often, and typically, in small wedge-shaped areas between well-formed laths of plagioclase, giving a typical 'intersertal' texture. It makes up about 20 % by volume (16 % by weight) of the whole rock, though its irregular distribution tends to reduce the accuracy of micrometric analyses. For the most part it is pale brown, clear, and isotropic, but here and there it is partly replaced by green anisotropic material, which is largely chloritic, and presumably formed by devitrification.

A small proportion (perhaps 1-2 % of the glass) is darker orange-brown in colour, and weakly birefringent. This substance—which shows more clearly in the crushed material prepared for analysis than in thin sections of the rock—is probably an oxidized and hydrated product of the glass itself, formed in a manner analogous with the alteration of sideromelane to palagonite.

The glass contains tiny inclusions. These are chiefly apatite, as needles and small prisms, but small crystals of pyroxene, felspar, and occasionally even of olivine, are found.

The concentrate for chemical analysis was prepared as follows. The rock was first crushed to pass a 120-mesh sieve, the finest rock flour washed away, and the powder, after drying at 100° C., was separated into light and heavy fractions with bromoform. The lighter fraction was rubbed gently in an agate mortar to break down as many composite grains as possible, and was then centrifuged in a bromoform-benzene mixture of specific gravity 2·6. This served to sink the felspar and felspar-rich composite grains, leaving a floating fraction rich in glass. By repeating the gentle rubbing and the centrifuging three times, a concentrate was obtained in which the only impurities were a trace of felspar and a few grains of the darker orange palagonitic material referred to above. Chlorite was entirely absent.

Microscope slides of the glass concentrate were prepared, and a grain count confirmed that the contamination by plagioclase in composite grains was certainly less than 2 %. Most of the inclusions of apatite are presumably still present in the glass concentrate, but the larger inclusions of other minerals were effectively removed by the crushing and centrifuging.

It may be mentioned in passing that considerable difficulty was experienced in washing out the last traces of bromoform from the glass

concentrate. Despite repeated washings with benzene and with ether, very slight traces of bromoform could be detected when the material was heated in an ignition tube. This substance must either be adsorbed very tenaciously on to the surface of the glass or else held in tiny cracks. Its presence means that the figure stated for H_2O at 110° in the analysis includes a trace of organic matter, though it is certainly not enough to affect the accuracy of the analysis significantly.

The results of the chemical analysis are given in table II (p. 57), together with others for comparison. The actual analysis of the glass concentrate is given in column IIa; in column II it has been corrected for the presence of 2 % of plagioclase of composition $Or_5Ab_{50}An_{45}$ (the value estimated from refractive index measurements) and recalculated to 100·00 %. It will be seen that allowance for this maximum estimated contamination of the analysed material by plagioclase makes very little difference indeed to the analysis. The 'corrected' analysis has already been given in table I, and has been used in all the other calculations and diagrams.

The refractive index and specific gravity were measured on the material separated for analysis. The bulk of the glass has a refractive index, determined by the immersion method, of 1·516. The material is not quite uniform, and there is a little variation in refractive index both above and below this figure, which is considered to be a good average. The specific gravity was determined by suspension in bromoform-benzene mixtures. Again, there is some slight variation above and below a central value, but the bulk of the material has a specific gravity of 2·43.

Correlation of physical properties with chemical composition.

The investigations of Tilley (1922) and George (1924) into the relationships between specific gravity, refractive index, and chemical composition of naturally occurring glasses were made on holohyaline rocks, yet it is interesting to see how they fit the results obtained for the Kinkell and Kap Daussy residual glasses. George (1924) has given curves relating refractive index to specific gravity, and refractive index to the content of the more important oxides in natural glasses. The values read from these curves corresponding to the measured refractive indices of the Kap Daussy and Kinkell residual glasses are given below, compared with the actual values obtained by direct chemical analysis.

The agreement is reasonably good, though both residual glasses are richer in lime than the curves would indicate, and the Greenland glass

	Glass from Kap Daussy tholeiite.		Glass from Kinkell tholeiite.	
	From George's curves.	From analysis.	From George's curves.	From analysis.
SiO_2	c. 65 %	64·0 %	c. 74 %	66·8 %
$FeO+Fe_2O_3$ ...	5·5	5·8	2·5	2·5
MgO	1·5	1·2	0·4	0·5
CaO	3·5	5·6	1·2	2·6
K_2O	3·8	1·5	4·1	4·2
Sp. gr.	2·51	2·43	2·33	2·38

is, of course, much poorer in potash. The results do suggest, however, that George's published curves may well be used to gain a fair idea of the composition of a residual glass of known refractive index in calc-alkaline rocks of the types here considered.

Tilley (1922) classified natural glasses on the basis of specific gravity and refractive index determinations, and found that by plotting specific gravity against specific refractivity the fields occupied by the various types of natural glasses are clearly delimited. If the specific refractivities $(K - (n-1)\,d)$ are calculated for the two residual glasses under discussion, and the values plotted on Tilley's curve (fig. 2 in his paper), it is found that the glass from the Kinkell tholeiite falls only just outside the field occupied by the rhyolite obsidians, as might be expected from its composition, while the Kap Daussy glass also falls outside this field, but falls within the field occupied by the 'australites'. These curious representatives of the tektite group of natural glasses are somewhat abnormal in composition, and are considered by many to be of meteoritic origin (cf. Spencer (1939), where all reliable physical and chemical data relating to them are collected together).

Chemical analyses of two tektites quoted from Spencer's paper are included in table II, and it will be seen that the Kap Daussy residual glass, which falls into Tilley's tektite field on the basis of physical properties, is also reasonably comparable in chemical composition. Scrutiny of Spencer's table of analyses shows that tektite glasses with refractive index and specific gravity comparable with the Greenland glass tend also to be relatively impoverished in alkalis and to have a relatively high content of iron oxides: most of this iron is usually in the ferrous state. Terrestrial volcanic glasses are usually chemically distinct from the tektites, and it is therefore of some interest to record the occurrence of a glass of terrestrial origin of closely comparable composition and having similar physical properties.

Tilley (1922) has further shown that a theoretical value for the specific refractivity of a glass can be calculated from the known (or inferred)

specific refractivities of the standard normative minerals in a glassy state. In many of the cases investigated he finds a close correspondence between these 'calculated' values and the 'observed' ones deduced from the measured specific gravity and refractive index ($K_{obs.} = (n-1)/d$). The discrepancy between observed and calculated values increases with the basicity of the glass and with its tenor of water (which has a high specific refractivity).

Such values have been calculated in the way indicated by Tilley for the two residual glasses, and are given below:

	K obs.	K calc.	K calc.– K obs.	K calc. (water free).
Kinkell glass	0·2079	0·2211	0·0132	0·2104
Glass from Kap Daussy tholeiite.	0·2124	0·2228	0·0104	0·2145

It will be noticed that the discrepancy between observed and calculated specific refractivities is of the order of 5 % in both instances, while agreement is really close if the calculation is based on 'water-free' analyses.

Chemistry of the residual glass.

The main features of the chemical analysis of the glass from the Kap Daussy tholeiite are a fairly high silica percentage, combined with low content of alkalis and relatively high content of iron and lime. As might perhaps be expected, the glass is rich in water—indeed the water content of the residual glass accounts for the greater part of the total water in the whole parent rock.

The composition of this glass is unusual. One would expect that it would be fairly comparable with rocks of corresponding silica percentage lying on the line of one or other of the igneous rock suites believed to be derived from the differentiation of a basaltic magma. Yet it is difficult to find analyses of other rocks which provide anything of a close comparison. As has already been mentioned, there is fairly close resemblance with two analyses of tektite glasses (analyses K and L, table II); Washington's tables of analyses (1917) provide only two comparable ones (F and G in table II), of which the dacite-pitchstone from Madagascar provides the closer comparison. From the British Tertiary province, two innimmorite-pitchstones from Mull provide the nearest comparable rocks. The analysis of one of these is given as analysis E in table II (p. 57).

It may perhaps be significant that the few rocks found which are more or less comparable in chemical composition with this residual glass are themselves glassy. This suggests that silicate solutions having these

somewhat unusual compositions may not crystallize very easily, so that a glassy product may be as much a function of chemistry as of the physical conditions obtaining at the time of consolidation.

The glass separated by Walker from the Kinkell tholeiite has more the composition which would be expected of the late differentiate of a basic magma. It is richer in alkalis than the Greenland one and much poorer in iron, lime, and magnesia. Walker remarks that, had it crystallized, the Kinkell glass would probably have yielded a micropegmatite, and in support of this he compares its composition with those of some of the granophyric segregation veins from the local dolerites, and with an acid vein from the Whin Sill (H and J, table II).

The most striking feature of the Kap Daussy glass, on the other hand, is its paucity in alkalis, particularly in soda. In fact there is a little less soda in the glass than in the parent rock, though potash has increased threefold and the total (K_2O+Na_2O) is rather higher. Such a glass could scarcely be expected to yield typical micropegmatite on crystallization, when there is only 9 % of normative orthoclase (as against 25 % in the Kinkell glass) and when the proportion of normative femic constituents is so much higher.

In this connexion it is perhaps relevant to remark that in another dike rock (E.G. 1120) from nearly the same locality there is a crystallized late mesostasis, consisting of acicular iron-ore crystals, tiny crystals of very strongly zoned plagioclase, chlorite, and small granules of a pyroxene, together with a little quartz and probably orthoclase in places, though the mesostasis is very fine grained and it is difficult to resolve the various minerals with the microscope. The rock itself is of the same general type as the one under discussion, and the proportion of mesostasis is about the same also. The nature of this crystalline mesostasis seems to indicate that in the earlier stages the residual liquid had still a fair proportion of lime and of iron (the abundance of magnetite indicates a high ratio Fe_2O_3:FeO). The strongly zoned plagioclase indicates that the liquid became enriched in soda only towards the very last stages in the crystallization.

The relationship between the chemical compositions of the Kap Daussy and Kinkell tholeiites and their residual glasses is shown diagrammatically in fig. 2. In this diagram the percentage of each oxide (along the ordinate) is plotted against the silica percentages of rock and glass (along the abscissa), cognate pairs of points being joined by arrows. It must be emphasized that these arrows are only 'tie-lines' and that there is no evidence of linear variation of each oxide with increasing silica.

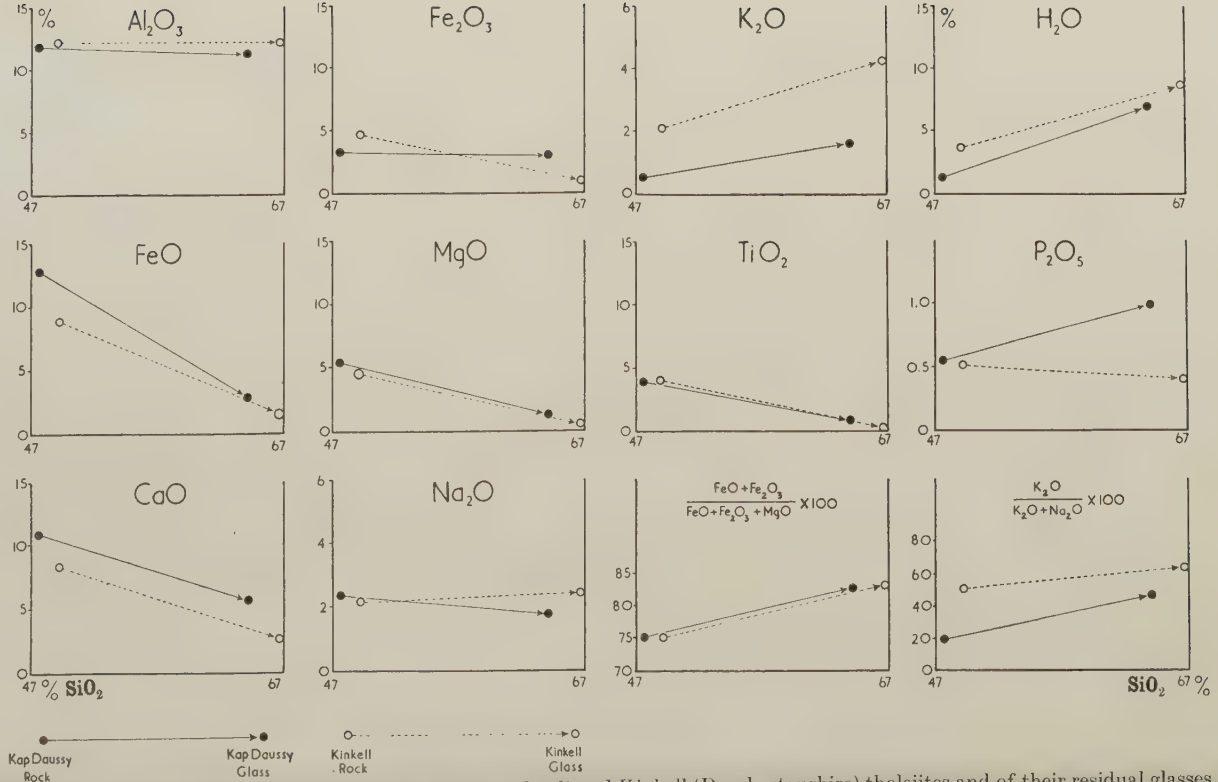

FIG. 2. Chemical composition of the Kap Daussy (Greenland) and Kinkell (Dumbartonshire) tholeiites and of their residual glasses.

It is quite surprising, however, that for the majority of the oxides these tie-lines for the Greenland and Kinkell rocks are very nearly parallel, indicating a close correspondence between the parent magma and its late residuum. In most cases the increase or decrease of a particular oxide from rock to glass is much the same for a corresponding increase in silica. For example, the tie-lines for CaO and total $FeO + Fe_2O_3$ (iron oxides are only shown separately in fig. 2) are strikingly parallel, with the line for the Kap Daussy tholeiite well above that for the Kinkell rock. Similarly, the K_2O lines do not diverge widely, the Kinkell line being well above the other. In a general way it is seen that iron oxides, magnesia, lime, and titania decrease to roughly the same extent for a similar increase in silica in both instances considered, while potash and water increase in the same way. Alumina and soda remain essentially steady.

In his earlier description of the Kinkell tholeiite, Walker (1930) remarks that Fenner believed the low refractive indices of certain residual glasses to be due, partly at least, to relatively high concentrations of phosphates, borates, and silicofluorides, the iron having escaped with the volatiles. The analyses of both the Kinkell and Kap Daussy glasses show them to be 'acid'. The latter has not been analysed for boron, but a spectrographic examination of the Kinkell rock showed less than 1 % B_2O_3, and Walker remarks (1930, p. 375) that it is extremely doubtful whether this would lower the refractive index of the glass. The amount of P_2O_5 in the Greenland glass, however, is nearly twice that in the parent rock. This is mainly due to tiny inclusions of apatite, but it is possible that there is still some phosphorus in solution in the glass. If this were in fact the case, it would tend to reduce the refractive index to a slight extent, since the specific refractivity of apatite (Tilley, 1922) is 0·201, slightly below the values given for most of the other normative minerals. The effect is probably negligible for the small amount of normative apatite which possibly remains occult in the glass.

Crystallization sequence of the Kap Daussy dike magma.

Although the known chemical composition of the residual glass from the Kap Daussy tholeiite provides tangible data for one point in the course of consolidation of the magma of this dike, it can, of course, give no direct information about the differentiation trend itself, only two points on the line being known. Comprehensive data are now available for the course of differentiation of several large masses of basaltic magma—for example, the Skaergaard intrusion (Wager and Deer, 1939)

TABLE I. Analyses of tholeiites and their residual glasses, with norms and modes.

Analyses.—	A.	I.	II.	B.	C.
SiO_2	47·35	47·42	64·03	49·10	66·80
Al_2O_3	13·90	11·75	11·27	12·13	12·10
Fe_2O_3	5·87	3·39	2·98	4·61	0·97
FeO	8·96	12·79	2·81	8·92	1·50
MgO	5·97	5·35	1·18	4·50	0·50
CaO	10·65	10·83	5·57	8·20	2·62
Na_2O	2·73	2·36	1·82	2·14	2·40
K_2O	0·54	0·55	1·56	2·10	4·20
$H_2O+110°$ ...	1·16	0·95	6·23	2·50	5·75
$H_2O-110°$ ...	1·04	0·30	0·73	1·02	3·00
TiO_2	1·75	3·98	0·79	4·02	0·18
P_2O_5	0·24	0·54	0·98	0·51	0·39
MnO	0·23	0·10	0·05	0·15	n.d.
Others ...	0·55	—	—	0·03	—
	100·94	100·31	100·00	99·93	100·41
Sp. gr. ...	2·96	$2·99_5$	2·43	—	2·38
Ratios.—					
$\frac{(FeO+Fe_2O_3)}{FeO+Fe_2O_3+MgO}\times 100$	75·0		82·9	75·0	83·2
$\frac{K_2O}{Na_2O+K_2O}\times 100$ ...	18·9		46·1	49·5	63·6

Norms.—	I.		II.		B.		C.	
qu		1·82		36·3		7·6		30·7
or	3·22		9·2		12·2		25·0	
ab	19·96	42·94	15·4	42·5	17·8	47·5	20·4	55·4
an	19·76		17·9		17·5		10·0	
di $CaSiO_3$	12·68		1·4				0·1	
$MgSiO_3$	6·01	25·19	0·9	2·7		15·8	0·1	0·3
$FeSiO_3$	6·50		0·4				0·1	
hy $MgSiO_3$	7·26	15·09	2·1	3·1		9·7	1·2	2·5
$FeSiO_3$	7·83		1·0				1·3	
mt		4·92		4·3		6·7		1·4
ilm		7·55		1·5		7·6		0·5
ap		1·28		2·3		1·3		1·0
Water		1·25		7·0		3·6		8·7
		100·04		99·7		99·8		100·5

Modes (% by volume).—	I.		B.	
Plagioclase	38·2	—	28·3	—
Augite	31·7	—	22·4	—
Hypersthene ...	—	—	7·0	—
Olivine	3·3	—	—	—
Iron ores	6·5	—	10·8	—
Mesostasis	20·3	—	31·5	—

A. Tholeiite of Salen type (Geol. Surv. No. 16808), dike, ¼ mile SSE. of Kintallen, Mull. Analyst, F. R. Ennos (quoted from Mull Memoir, Bailey, 1924, p. 17).

I. Olivine-tholeiite dike (E.G. 1123), Kap Daussy, east Greenland. Analyst, E. A. Vincent (new analysis).

II. Residual glass from olivine-tholeiite E.G. 1123. (Analysis IIa in table II corrected for presence of 2 % felspar and recalculated to 100·00 %). Analyst, E. A. Vincent (new analysis).

B. Tholeiite dike of Upper Carboniferous age, Kinkell quarry, Kirkintilloch, Dumbartonshire. Analyst, J. Jakob (quoted from Walker, 1930, p. 368).

C. Residual glass from Kinkell tholeiite. Analyst, F. Herdsman (quoted from Walker, 1935, p. 150).

TABLE II. Analyses of residual glasses with comparisons.

	IIa.	II.	IIb.	C.	D.	E.
SiO_2	63·96	64·03	68·82	66·80	65	62·37
Al_2O_3	11·60	11·27	12·11	12·10	12	12·04
Fe_2O_3	2·93	2·98	3·20	0·97	6	1·87
FeO	2·76	2·81	3·02	1·50		5·81
MgO	1·16	1·18	1·27	0·50	1·7	0·97
CaO	5·65	5·57	5·99	2·62	3	3·51
Na_2O	1·91	1·82	1·96	2·40	3·5	3·47
K_2O	1·55	1·56	1·68	4·20	3	2·34
$H_2O+110°$ ...	6·12	6·23	—	5·75	—	5·54
$H_2O-110°$ ...	0·72	0·73	—	3·00	—	0·44
TiO_2	0·78	0·79	0·85	0·18	—	1·06
P_2O_5	0·96	0·98	1·05	0·39	—	0·30
MnO	0·05	0·05	0·05	n.d.	—	0·24
Others ...	—	—	—	—	—	0·07
	100·15	100·00	100·00	100·41	—	100·03
Sp. gr. ...	2·43	—	—	2·38	—	—
Refr. index	1·516	—	—	1·495	—	—

	F.	G.	H.	J.	K.	L.
SiO_2	68·45	62·63	69·57	65·20	69·32	70·62
Al_2O_3	10·00	12·19	13·03	13·72	12·27	12·34
Fe_2O_3	5·71	2·98	0·98	3·63	0·06	2·25
FeO	2·59	2·89	3·59	3·72	6·81	3·17
MgO	3·26	1·49	1·06	1·01	4·05	3·61
CaO	6·20	4·84	1·56	2·79	3·72	2·99
Na_2O	1·98	2·12	4·57	5·22	0·77	1·68
K_2O	1·18	0·82	2·37	2·17	2·18	1·57
$H_2O+110°$ ...	0·62	4·11	2·04	1·27	—	—
$H_2O-110°$ ...	0·18	3·94		0·72	—	—
TiO_2	0·20	1·53	0·65	0·39	—	—
P_2O_5	0·25	0·35	0·47	0·38	—	—
MnO	0·05	—	—	n.d.	—	—
Others ...	—	—	0·89	—	—	—
	100·67	99·89	100·78	100·22	—	—
Sp. gr. ...	—	—	—	—	2·498	2·442
Refr. index	—	—	—	—	1·526	1·51

IIa. Glass concentrate separated from tholeiite (E.G. 1123), Kap Daussy. Analyst, E. A. Vincent (new analysis).

II. Analysis IIa, corrected for 2 % plagioclase contamination.

IIb. Analysis IIa, calculated water free.

C. Residual glass from Kinkell tholeiite, Dumbartonshire (Walker, 1935).

D. Normal Mull magma series for 65 % SiO_2.

E. Inninmorite-pitchstone, ½ mile SW. of Pennyghael, Mull (Anderson and Radley, 1915).

F. Granite-gneiss, Fredericksburg, Virginia (Washington's Tables, p. 332).

G. Dacite-pitchstone, Morateno, Madagascar (Washington's Tables, p. 332).

H. Segregation vein in quartz-dolerite, Fifeshire (Day, 1928, quoted in Walker, 1935).

J. Felsitic vein in Whin Sill, Alnwick Moor, Northumberland (Tomkeieff, 1929).

K. 'Tektite', Martapoera, Borneo (quoted in Spencer, 1939).

L. 'Tektite', Kalisso, Java (quoted in Spencer, 1939).

and the Karroo dolerites (Walker and Poldervaart, 1949), among others, and less definite data from Mull (Bailey, 1924)—but positive data of a similar kind for various stages during the crystallization of a small body of magma in, say, a dike or a sill, are still needed. We cannot, of course, hope to be able to follow the process of crystallization-differentiation at all easily in these small intrusions, but further chemical data even on their late stage residua, where these can be separated, would be very valuable. It is worth while, however, to see how this one residual glass compares with one or two of the well-known differentiation series of rocks commonly believed to be derived from basaltic magmas.

First, there is the normal Mull magma series, regarded by the authors of the Mull Memoir (Bailey, 1924) as a series resulting from the crystallization-differentiation of a parent basaltic magma. The Kap Daussy tholeiite analysis (analysis I, table I) fits fairly well on the variation diagram (fig. 2 in the Mull Memoir) for the normal Mull magma series at 47 % SiO_2. Its glassy residuum, however, cannot be made to fit into this same series at 64 % SiO_2. The discrepancies—high lime, low alkalis—are evident when the glass analysis is compared with columns D and E in table II. The Mull variation curves are supported by many analyses, and it is evident that the Kap Daussy glass simply does not belong to a comparable differentiation series: it does not show sufficient enrichment in alkalis.

An admirable summary of the trends of differentiation in basaltic magmas has recently been given by Walker and Poldervaart (1949, pp. 650–665) who believe, with Wager and Deer, that the normal course of differentiation leads to iron enrichment in the early and middle stages, and enrichment in silica and alkalis towards the end. In contrast to such a series (exemplified by the Skaergaard magma) is the ordinary calc-alkaline series, represented by Daly's average basalt, andesite, dacite, and rhyolite, and by the rocks of the Garabal Hill–Glen Fyne complex (Nockolds, 1941). Wager and Deer (1939) believe this latter calc-alkaline series to be in the main derived from mixing acid and basic materials; while Nockolds considers the Garabal Hill series to be an example of straight crystallization-differentiation. Walker and Poldervaart (1949, p. 661) 'consider it likely that the calc-alkaline suite may be produced by fractionation of basalt magma, though they do not exclude the possibility of assimilation of sialic material, followed by crystallization-differentiation of the hybrid magma'.

To illustrate these contrasted differentiation series, Wager and Deer made use of a triangular diagram to plot FeO, MgO, and $K_2O + Na_2O$. This method is adopted by Walker and Poldervaart, who give a series of such diagrams to illustrate a number of magmatic series.

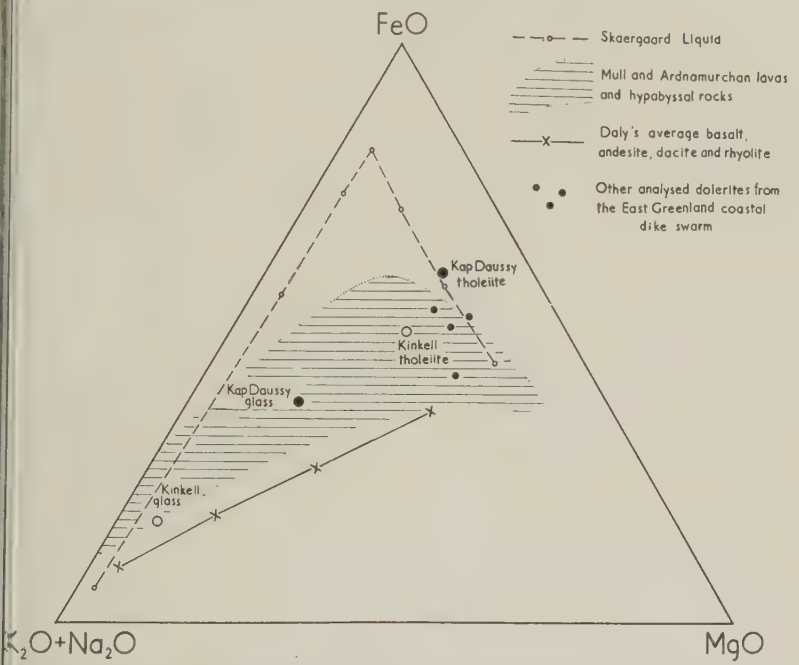

FIG. 3. Relation of the Kap Daussy and Kinkell tholeiites and residual glasses to the differentiation trends of the Skaergaard (Greenland) and calc-alkaline series.

If the Kinkell tholeiite and its glass and the Kap Daussy tholeiite and its glass are plotted on such a diagram (fig. 3), it is seen that the former glass lies close both to the Skaergaard trend and to the calc-alkaline trend where these converge towards the $(K_2O + Na_2O)$ corner of the triangle, though its parent rock is not particularly close to either trend. The Kap Daussy tholeiite itself falls in this diagram practically on the line for the Skaergaard series, and the four other dolerites from the east Greenland coastal dike swarm so far analysed are also fairly close to this line. Most of the Mull and Ardnamurchan lavas and basic hypabyssal rocks fall slightly nearer to the $(K_2O + Na_2O)$ corner of the triangle than do the Greenland rocks.

The residual glass from the Kap Daussy tholeiite, however, occupies

a curious position midway between the two trends, and although on this diagram it lies inside the field occupied by the Mull series, it is rather isolated there, its nearest neighbours being two inninmorite-pitchstones and two leidleites. The FeO–MgO–(K_2O+Na_2O) diagram, satisfactory as it is for showing the main differentiation trends, does not suit the Kap Daussy residual glass particularly well, as it takes no account of percentages of silica or of lime.

It has been found that the ratios

$$(FeO+Fe_2O_3)/(FeO+Fe_2O_3+MgO)\times 100 \quad \text{and} \quad K_2O/(K_2O+Na_2O)\times 100$$

provide useful criteria of differentiation in series of rocks derived from basaltic magma (cf. Wager and Deer, 1939, pp. 299–305; Walker and Poldervaart, 1949, p. 652), and are certainly of more fundamental significance than silica percentage. The 'iron ratio' is useful for the earlier stages and the 'alkali ratio' for the later ones. These ratios have been calculated for the rocks and glasses considered here, and are plotted against silica percentages in fig. 2. Once again the tie-lines are nearly parallel. Using the ratio $(FeO+Fe_2O_3)/(FeO+Fe_2O_3+MgO)\times 100$ as a criterion, the two glasses seem to have differentiated from their parent rock magmas to much the same extent, while the Kap Daussy glass shows a rather more marked concentration of potash in the total alkalis. Referring to fig. 2, it is seen that the various diagrams could equally well have been plotted with the ratio

$$(FeO+Fe_2O_3)/(FeO+Fe_2O_3+MgO)\times 100$$

as the abscissa (instead of percentage SiO_2), and the parallel arrangements of the tie-lines would still be evident.

Whether silica percentage or iron ratio is used as a measure of differentiation, then, it seems that the course of crystallization in the Kinkell and Kap Daussy dike magmas may have been rather similar, the end-product represented by the residual glass depending upon this course as well as upon the composition of the parent magma. In this connexion, the diagram for P_2O_5 in fig. 2 is of some interest. The Kap Daussy glass with its inclusions of apatite, which together represent the residual magmatic solution, is enriched in phosphorus, while the Kinkell glass contains less phosphorus than its parent rock. In the Skaergaard magma it was found that the P_2O_5 content increased steadily through the differentiation series until the later stages, when it fell suddenly and rapidly. A similar effect may be taking place in the Kap Daussy dike magma, this particular residual solution representing a stage at

which the concentration of phosphorus was around the maximum. Had the residuum represented, say, only about 10 % of the magma, it may well have been quite poor in P_2O_5, as is the Kinkell glass.

This point lends some support to the view that if the Kap Daussy glass represented a smaller proportion of its parent magma, it might approach the more ordinary composition of the Kinkell glass somewhat more closely, although the characters inherited from the parent magma —high iron oxides and lime, and low potash— persist to a relatively late stage in the present glass, and it seems unlikely that an even later stage residuum would be really close to the Kinkell glass in composition.

There is insufficient evidence to show whether or not the course of differentiation of the Kap Daussy dike magma has followed the characteristic iron-enrichment trend shown by the Skaergaard magma and the Karroo dolerites, and it does not appear either to have followed closely the trend of the normal Mull magma series. It appears to have followed a rather unusual course which did not lead to a residual magma of granitic composition. Further separation and analysis of similar residual glasses is much needed in order to try to establish the trends of the later stages of crystallization-differentiation in small intrusions of the kind considered here.

Acknowledgements.—The Kap Daussy material was collected by L. R. Wager during the Scoresby Sound Committee's second east Greenland expedition, 1932, under the leadership of Capt. Ejnar Mikkelsen. The writer wishes to thank Professor Wager for providing specimens of this rock, and for his encouragement and helpful criticism throughout the work.

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Pisanite from Parys Mountain, Anglesey.

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[Communicated by Prof. W. J. Pugh; read November 10, 1949.]

DURING the Manchester University's 1946 geological excursion to Anglesey, a visit was made to Parys Mountain. At this locality small quantities of an attractive light blue mineral were found capping pyrite veins and in clefts in the rock. Larger finds were obtained in an artificial cavern which extended for fifty or sixty feet into the south-east side of the excavated pit. A specimen weighing $2\frac{1}{2}$ pounds and consisting of silicified shale veneered with the pale blue mineral was collected by the author and examined in the geological research laboratory at Manchester University during the session 1948-1949. The blue mineral was identified as pisanite, and this is the first record of pisanite as a British mineral.

Parys Mountain is situated in the north-west of Anglesey close to Amlwch. Copper and to a smaller extent lead were mined throughout a period exceeding one hundred and fifty years, but operations have completely ceased since the first world war. The geological structure of the district need only be briefly outlined for the purpose of this study. Upper Ordovician shales (Parys Green Shales) are separated by a thick felsite sill from Lower Silurian shales (Llandovery), all the beds being folded isoclinally so that the limbs dip steeply north-north-west. The shales are finely cleaved and the area is cut by several major faults, one of which (Rhwms thrust plane) underlies much of Parys Mountain. Post-Silurian metasomatism gave rise to the rich and varied assortment of minerals to be found in this locality, and Greenly[1] envisages three distinct phases of metasomatism. At first the fine-grained shales and the felsite dike were silicified to such a degree that, commonly, the silicified shales comprise nothing but minute interlocking quartz grains. The latter show no sign of stresses or straining and are indicative of the younger age of silification with respect to Silurian earth movements. A second period of metasomatism saw the introduction of micaceous material, whilst the third period witnessed the incoming of pyrite and associated metallic ores.

[1] E. Greenly, The geology of Anglesey. Mem. Geol. Surv., 1919, vol. 2, pp. 561 and 823. [M.A. 1-328.]

Among the twenty-six minerals listed by Greenly as occurring at Parys Mountain mention is made of melanterite and hydro-glockerite, but data for these minerals were not published. There is no reference to pisanite in his memoir. The mineral described here is not likely to have been Greenly's melanterite, because it had obviously grown within recent years and, in addition, no search was made to prove or disprove the presence of true melanterite.

The mineral here described was found as a fungus-like growth in clefts and artificial cavities. Blasting of the rocks had left several large caverns in which percolating water had given rise to the recent development of pisanite capping pyrite veins and forming stalactites from overhanging ledges. The country-rock is a completely silicified shale which, under the microscope, reveals a mass of closely interlocking quartz grains cut by many quartz veins. The quartz veins carry innumerable cubes of pyrite and grains of chalcopyrite, many of which are surrounded by a halo of sericite crystals.

In the hand-specimen the pisanite is seen to be a pale blue mineral of crystalline nature but indeterminate crystal morphology. Closest to the flinty country-rock the pisanite is blue in colour, but farther away from the contact it becomes dirty green and is generally coated with a sulphur-yellow, dust-like mineral. The yellow mineral is found as tiny amorphous flecks and, rarely, as small glassy nodules. Although an accurate determination of the crystal morphology of this pisanite is impossible, due to the small and poorly developed crystals, the general crystal form can be made out. The most characteristic feature is the acicular nature of crystals with elongation parallel to the *c*-axis and flattening on the (010) face. A good cleavage parallel to (001) can also be observed in the hand-specimen. The acicular crystals are sometimes a quarter of an inch long but no thicker than a needle, and where packed closely together the pisanite has a decidedly fibrous appearance.

So far as was possible, pisanite was separated from yellow mineral, but as is inevitable when minerals are very closely intergrown, a small proportion of the yellow mineral was analysed along with the pisanite and presumably gives rise to the presence of some of the ferric iron. Water of crystallization was determined by heating at about 380° C. for 10 hours. This sufficed to obtain a constant weight. Less water of crystallization is present than a theoretical consideration demands (only 93·95 % theoretical water –due to partial dehydration during storage in a warm, dry room). The chemical composition of Parys Mountain

pisanite is summarized in table I. Insoluble matter was determined separately for each sample used and the analyses were corrected accordingly.

TABLE I. Chemical analysis of pisanite from Parys Mountain.

	%	Mol.% × 1000.	$FeSO_4.7H_2O$.	$CuSO_4.7H_2O$.	Diff.
SO_3 ...	28·89	361	233	122	+6
FeO ...	16·83	233	233	—	—
Fe_2O_3 ...	2·05	13	—	—	+13
CuO ...	9·72	122	—	122	—
H_2O ...	42·69	2360	1631	854	−125
	100·18		64·4 %	34·7 %	
Sp. gr.	1·90				

For purposes of comparison the chemical analyses of some other pisanites are reproduced in table II.

TABLE II. Selection of previous analyses of pisanite.

	1.	2.	3.	4.	5.	6.	7.	8.
SO_3	29·90	28·8	29·18	29·25	27·33	28·18	28·98	28·66
FeO	10·98	8·5	16·47	5·46	17·23	13·43	19·67	15·08
CuO	15·56	19·2	9·22	17·95	8·21	11·67	4·82	11·51
H_2O	43·56	44·9	45·74	45·21	46·96	46·72	44·76	44·70
	100·00	101·4	100·61	100·69	100·00	100·00	99·77	100·30

1. The original pisanite from Turkey. F. Pisani, Compt. Rend. Acad. Sci. Paris, 1859, vol. 48, p. 807.

2. Sain-Bel, Rhône, France. A. Lacroix, Min. France, 1910, vol. 4, p. 229.

3, 4. Leona Heights, Alamada Co., California. W. T. Schaller, Bull. Dept. Geol. Univ. California, 1903, vol. 3, p. 199. Extreme values of three analyses. Insoluble residue deducted. In analysis 4 also MgO 2·82 %.

5, 6. Lading, Carinthia. H. Leitmeier, Centralblatt Min., 1917, p. 231. In analysis 5 also NiO 0·27 %. [M.A. **1**-347.]

7, 8. Rio Tinto, Spain. H. F. Collins, Min. Mag., 1923, vol. 20, p. 32. Extreme values of four analyses, a fifth partial analysis shows CuO 17·54 %. In analysis 7 also MnO 0·31 %, ZnO 1·13 %, (Ni,Co)O 0·10 %. In analysis 8 also ZnO 0·35 %.

Standard works give the optical properties of melanterite ($FeSO_4.7H_2O$), pisanite ($(Fe,Cu)SO_4.7H_2O$), and boothite ($CuSO_4.7H_2O$), and table III tabulates the properties of these minerals as recorded by Dana[1] and Winchell[2]. The last column shows the optical properties of Parys Mountain pisanite as determined by the writer.

[1] E. S. Dana, A textbook of mineralogy. 4th edition, 1932, pp. 761–762. [M.A. 5–193.]

[2] A. N. Winchell, The microscopic characters of artificial inorganic solid substances or artificial minerals. 2nd edition, 1931, pp. 231–232. [M.A. 5–2.]

TABLE III. Optical and physical data.

	Melanterite, $FeSO_4.7H_2O$.	Pisanite, $(Fe,Cu)SO_4.7H_2O$.	Boothite, $CuSO_4.7H_2O$.	Pisanite, Parys Mtn.
Angle β ...	75° 45′	74° 38′	74° 24′	75° 12′
Refr. indices α	1·471	1·472	near those	1·471
Refr. indices β	1·478	1·479	of	—
Refr. indices γ	1·486	1·487	pisanite	1·487
Optic sign	+	+	+or−.	+
2V	85° 27′–86°	very large	90°	87°
Opt. ax. pl.	(010)	(010)	(010)	(010)
$\alpha : c$ ...	29°	22°	about 15°	26°
Cleavage	(001) perfect (110) less so	(001) perfect	(001)	(001)
Sp. gr. ...	1·89–1·90	1·9	2·1	1·90
Colour ...	green	pale blue	blue	pale blue

As the optical properties of pisanite and melanterite are almost identical it is difficult to name the Parys Mountain pisanite without reference to a chemical analysis. Microscopical examination of the pisanite indicates that the green colour of exposed mineral is largely due to the included fragments of yellow alteration mineral which occurs only on the outer exposed edge of the crystalline pisanite mass. The pisanite itself is derived by hydration and oxidation from pyrite; further weathering produced the yellow alteration mineral.

Under the microscope, the yellow mineral is seen to be an amorphous material with some measure of birefringence or a cryptocrystalline mineral of very low birefringence. It is pale yellowish-green in colour, honey-yellow in reflected light, and has a refractive index in the vicinity of 1·732. It is soluble both in water and carbon bisulphide. A yellow ferric sulphate from Parys Mountain was analysed by A. H. Church[1] who gave it the formula $2Fe_2O_3.SO_3.8H_2O$. This formula is similar to that of glockerite but with more water, and E. Greenly (loc. cit.) applied to it the name hydro-glockerite. Church stated that the mineral was crystalline and seemed to be isotropic. Whether this is identical with the yellow mineral now described is uncertain. As insufficient yellow mineral was available for chemical analysis its true nature must remain unknown.

A few minute crystals of a chestnut-brown alteration mineral have also been noticed, but not identified. These crystals may possibly be römerite $FeSO_4.Fe_2(SO_4)_3.14H_2O$.

Some thirty compounds having the general formula $xFe_2O_3.ySO_3.zH_2O$ have been listed[2] and the system Fe_2O_3–SO_3–H_2O has been studied

[1] A. H. Church, Min. Mag., 1895, vol. 11, p. 13.

[2] F. K. Cameron and W. O. Robinson, Journ. Phys. Chem., 1907, vol. 11, p. 641.

in detail[1]. These researches indicate that a high degree of solid solution occurs between the three primary components and most of the binary and ternary compounds, so that the existence of phases is possible, the physical properties of which differ from those of definitely fixed compounds.

[1] E. Posnjak and H. E. Mervin, Journ. Amer. Chem. Soc., 1922, vol. 44, p. 1965.
[M.A. 2–21.]

A note on the crystallography of epidote.

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[Communicated and read by Dr. M. H. Hey, November 10, 1949.]

IN any monoclinic crystal, the zone-axis $[uvw]$ is perpendicular to the plane (hkl) if $u/(hc^2-lac\cos\beta) = v/(kc^2a^2\sin^2\beta) = w/(la^2-hac\cos\beta)$. In particular, the normal to the face (100) is quasi-parallel to the zone-axis $[r0\bar{1}]$ if $c/(a\cos\beta)$ approximates to a rational number r.

Epidote has $a:b:c = 1{\cdot}5807:1:1{\cdot}8057$, β 115° 24′, and is often twinned on $a(100)$. G. Friedel[1] describes and explains these twins in terms of a pseudo-normal zone-axis [301], with an obliquity of 3° and a twin-index 3. But the choice of a pseudo-normal zone-axis is necessarily arbitrary, since it is always possible to find a rational zone-axis making an angle with any given face-normal less than any assigned angle δ: though the indices of such an axis may involve large numbers. Friedel prefers 'simple' indices, but does not give a strict definition of this term.

Now the zone-axis [803] makes an angle of only 1½′ with the normal to (100), and the (100)-twins of epidote can therefore be described in terms of a pseudo-normal zone-axis [803] with an obliquity of 1½′ and a twin-index 4, and we think this description is preferable.

For consider, in an arbitrary monoclinic crystal a face (hkl) cutting the crystallographic axes and the zone-axis [803] in the points H, K, L, and P respectively. Producing PO to P' and making $OP' = OP$, construct the plane $(h'k'l')$ through the points P', K, and L. Then $h' = -4h-3l$, $k' = 4k$, and $l' = 4l$. If now the zone-axis [803] is perpendicular to (100), the faces (hkl) and $(h'k'l')$ are related to one another as mirror-images in the plane (100). Hence in epidote pairs of faces reciprocally related by the transformation $\bar{4}0\bar{3}/040/004$, as, for example, (011) and $(\bar{3}44)$, will display this special orientation so exactly that goniometrical measurement will disclose no disagreement.

A scrutiny of O. Matthes's[2] angle-table shows that there are many such pairs of forms (see table I) among the 119 'gesicherten typischen Formen des Epidots' listed by him. Remembering that twins on (100) are very common with epidote, one sees that there is room for doubt in

[1] G. Friedel, Bull. Soc. Industrie Minérale, 1904, ser. 4, vols. 3–4, p. 399.

[2] O. Matthes, Neues Jahrb. Min., Abt. A, 1928, Beilage-Band 56, p. 418. [M.A. 4–88.]

assigning indices to many faces. For instance, the faces ($\bar{1}\bar{1}$.0.4) and ($\bar{7}$04) might well be (201) and (101) respectively, of a twinned portion of the crystal. We conclude that a number of the 119 forms listed by Matthes need verification by methods other than gonimetrical measurement, for example, etching, or epitaxy of suitable chemical compounds.

TABLE I. Pairs of faces symmetrical about (100) and liable to confusion in twinned crystals.

(The numbers in column 1 are those of the crystal-forms in O. Matthes's angle-table.)

No.	ϕ.	ρ.	Symbol.
1	64° 36′	90°	(001)
44	115° 20′	90°	($\bar{3}$04)
15	64° 36′	31° 30′	(011)
103	115° 25′	31° 30′	($\bar{3}$44)
17	18° 25′	90°	(201)
67	161° 35′	90°	($\bar{1}\bar{1}$.0.4)
18	22° 52′	90°	(302)
63	157° 7′	90°	($\bar{9}$04)
20	25° 56′	90°	(504)
62	154° 2′	90°	($\bar{2}$01)
21	29° 54′	90°	(101)
60	150° 5′	90°	($\bar{7}$04)
23	35° 5′	90°	(304)
56	144° 53′	90°	($\bar{3}$02)
26	42° 5′	90°	(102)
51	137° 53′	90°	($\bar{5}$04)
30	51° 39′	90°	(104)
47	128° 18′	90°	($\bar{1}$01)
33	80° 59′	90°	($\bar{1}$04)
35	98° 57′	90°	($\bar{1}$02)
75	29° 54′	48° 0′	(111)
107	150° 5′	48° 0′	($\bar{7}$44)
81	128° 18′	35° 12′	($\bar{1}$11)
99	51° 39′	35° 13′*	(144)
98	42° 5′	39° 33′	(122)
104	137° 53′	39° 33′	($\bar{5}$44)

* Matthes made here an error in his calculations and gives 35° 2′.

In the course of the goniometrical investigation of a very beautiful epidote crystal (47 × 7 × 2 mm., figs. 1 and 2) from Sulzbachthal, Salzburg, we found the forms (100), (001), ($\bar{1}$04), ($\bar{1}$02), ($\bar{3}$04), ($\bar{1}$01), ($\bar{7}$04), ($\bar{1}$03), ($\bar{2}$01), ($\bar{3}$01), (210), (110), (010), (012), (011), (144), (111), ($\bar{3}$44), ($\bar{1}$11), and ($\bar{7}$44), all with values of ϕ and ρ in excellent agreement with the values cited by Matthes. But we also observed two faces at ϕ 16° 45′, ρ 90° and ϕ 115° 22′, ρ 50° 48′ (zone adjusted, [010]), which do not

appear in Matthes's table; the faces ($\bar{3}01$) and (012), however, have positions ϕ 163° 14′, ρ 90° and ϕ 64° 36′, ρ 50° 48′ respectively, and are therefore the mirror-images of our observed faces in (100). Further, we observed the rare face ($\bar{3}04$) with a considerable expanse.

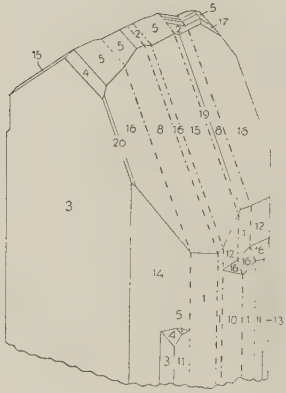

Fig. 1

Fig. 2

Fig. 1. Epidote crystal from Sulzbachthal, Salzburg.

Fig. 2. Orthographic projection of the same on the plane (010).

The lines — · — · — · represent re-entrant or salient twin-edges, while — — — — are twin-boundaries on a plane face (nos. 5. 5; 1, 11; 2, 2). The faces are numbered as follows: 1 (001), 2 (010), 3 (100), 4 (210), 5 (110), 6 (120), 7 (012), 8 (011), 9 (101), 10 ($\bar{1}02$), 11 ($\bar{3}04$), 12 ($\bar{1}01$), 13 ($\bar{2}01$), 14 ($\bar{3}01$), 15 (111), 16 ($\bar{1}11$), 17 ($\bar{2}21$), 18 ($\bar{1}71$), 19 ($\bar{2}33$), 20 ($\bar{2}11$), 21 ($\bar{2}.13.2$).

These observations are readily explained if we assume that our crystal, though apparently simple, is really twinned, and that the above two forms are ($\bar{3}01$) and (012) of a twinned part of the crystal; also, the supposed ($\bar{3}04$) may be really (001) of a twinned part. Working on these lines, and exploring diligently for re-entrant edges and other hints (striations, &c.), we were able to explain our crystal by supposing it to consist of a twin-group of at least six parts. Several of the faces mentioned above then get simpler indices: ($\bar{1}04$) → ($\bar{1}02$), ($\bar{7}04$) → (101), (144) → ($\bar{1}11$), ($\bar{3}44$) → (011), ($\bar{7}44$) → (111).

A close inspection yielded a harvest of very small facets belonging to

the forms (120), ($\bar{2}21$), ($\bar{1}71$), ($\bar{2}33$), ($\bar{2}11$), and ($\bar{2}.13.2$). The last-named is not in Matthes's table, but the face gave a good reflection with ϕ 128° 20′, ρ 6° 14′ (calculated from the above elements, ϕ 128° 18′, ρ 6° 12′); it has, however, been previously recorded, on two crystals from Sulzbachthal studied by H. Bücking.[1]

[1] H. Bücking, Zeits. Kryst. Min., 1878, vol. 2, pp. 339 and 409.

Trioctahedral minerals in the soil-clays of north-east Scotland.

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[Read at the meeting of the Clay Minerals Group, November 11, 1949.]

THIS paper deals with a series of soil-clay minerals which have a widespread distribution in the north-east of Scotland. The original member is a biotite-like mica which breaks down readily in the soil into (i) a vermiculite or (ii) a montmorillonite, depending on the soil-forming conditions operating. Apart from this 'clay biotite' and its decomposition products, the main crystalline constituents of the Scottish soil-clays are a member of the kaolinite group and illite ('clay muscovite'). Iron and aluminium oxides are present in all the clays in the amorphous condition, but crystalline varieties are scarce. The distribution of the minerals and their relationship to the various soil-forming factors will form the subject of a separate communication; here, the nature of the clay minerals and their interrelationships are considered.

Apparatus.

The present work has been carried out mainly by means of X-ray diffraction, supplemented wherever possible by other methods. X-rays were generated from a continuously-evacuated self-stabilizing gas tube, Fe-$K\alpha$ radiation being used throughout because of the large amounts of iron present in the soil-clays and the consequent excitation of secondary radiation with primary copper radiation. The focus on the target was such that the maximum output of the tube was 37 kilovolts, 10 milliamps, if holing of the target face was to be avoided. With this arrangement, well-exposed powder photographs were obtained in 12–18 hours. 9-cm. cameras of a modified commercial type and similar to those described by MacEwan (1) were used and were evacuated to about 2 cm. Hg during operation. Adjustments made to the slits of the collimating systems ensured that diffractions up to 35 Å. could be measured. Back-scatter from the undeflected beam was prevented by fitting directly on to the back of the film at the exit hole a readily removable lead shield with a hole coincident with but of slightly smaller size than that in the film.

Nomenclature.

The terms trioctahedral and dioctahedral were proposed by Stevens (2), the former to designate layer minerals in which all possible octahedral positions are occupied and the latter for those in which one in three octahedral positions are vacant. As applied to the members of the mica group they are interchangeable with the better-known terms octophyllite and heptaphyllite (3) respectively. Outside the mica group, however, the terms are not necessarily equivalent, since talc and vermiculite, for example, are trioctahedral minerals although they are not octophyllites.

The difficulty of differentiating between the various micas by means of X-ray powder diffraction alone has been pointed out by Nagelschmidt (4). As he has shown, however, there are distinct differences between the muscovite and phlogopite-biotite type of powder diagram, that is to say, between the diagrams of dioctahedral (or heptaphyllite) and trioctahedral (octophyllite) micas. Perhaps the most important difference between the two groups lies in the position of a well-marked reflection which, in the dioctahedral members, always occurs at about 1·49–1·51 Å. and, in the trioctahedral types, at 1·53–1·55 Å. (We shall refer to this reflection for simplicity as the (060), although other sets of indices may also be assigned to it.)

From an examination of the powder diagrams of trioctahedral and dioctahedral minerals not of the mica group it appears that this relationship is a general one for layer-lattice silicates, which can be classed in most cases as trioctahedral or dioctahedral from the position of their (060) line (or (06) line, in the case of the 'two-dimensional' structures). The maximum range of position of this line in dioctahedral minerals is about 1·485–1·520 Å. and, in trioctahedral types, 1·515–1·560 Å. A (060) spacing greater than 1·52 Å. is thus a fairly definite indication of a trioctahedral mineral, and one less than 1·51 Å., of a dioctahedral type. Use is made of this relationship in the present paper in describing certain of the soil-clay minerals, which are classed as trioctahedral solely from the position of this line on the diffraction diagram, since reliable chemical data on the pure minerals are very difficult to obtain.

The trioctahedral mica.

X-ray photographs of Scottish soil-clays frequently show at about 1·53 Å. a medium to strong reflection forming a part of the diffraction pattern of a micaceous mineral or its decomposition products. Occasionally the associated first-order basal reflection at 10 Å. is sharp and

due to the presence of an unweathered mica; although more generally the reflection is diffuse, or it may be displaced to a different position, because of the readiness with which the 10 Å. mineral breaks down in the soil. The diffraction diagram of the unweathered mineral is given in table I. In its trioctahedral nature, this soil-clay mica differs from all the micaceous constituents of clays so far described which appear to be exclusively dioctahedral types.[1] From its powder pattern it would seem to bear the same relation structurally to biotite as dioctahedral illite does to muscovite (fig. 1).

Table I. X-ray diffraction diagram of the trioctahedral clay mica (Fe-$K\alpha$).

dÅ.	$I_{est.}$	Indices.	dÅ.	$I_{est.}$	Indices.
10·0	10	002	2·41	4	133, 203
4·94	2	004	2·158	2	135, 205
4·47	9	020, 110	1·982	1	0010
3·68	2 b	113, 023	1·689	3	0012 &c.
3·32	9	006	1·649		
3·16	0·5	114	1·530	6	060, 330
2·86	1	115	1·446	0·5	
2·60	6	200, 13$\bar{1}$	1·320	0·5	400
2·50	1	008			

b = broad.

The name *illite* was proposed in 1937 by Grim, Bray, and Bradley (5) as a group name for all the micaceous constituents of clays, with the reservation that it might be desirable at some future date to re-define the term so as to restrict it to a particular type of clay mica. So far, the term has been applied to micas of the muscovite type only, and it may eventually be found convenient to use illite in this sense alone, in which case the term could not be applied to the trioctahedral clay mica. On the other hand, if illite is to be adopted as a group name for all clay micas, then the trioctahedral mica of the Scottish soil-clays would be classed as a *trioctahedral illite*. In view of the present indefinite meaning of the term illite, the soil-clay mica will be referred to in the present communication as the *trioctahedral clay mica* or simply as 'clay biotite'.

The possibility has been considered that the name *pholidolite* might be used, since Hendricks (6) has suggested that this mineral might be the degraded trioctahedral mica equivalent to the dioctahedral illite. Pholidolite, however, is an imperfectly defined mineral described by

[1] Recently MacEwan (1) has noted the existence of a trioctahedral mica in certain Scottish soil-clays.

Nordenskiöld (7) found only in drusy cavities in certain Swedish rocks, and is not essentially a clay mineral.[1] Similarly, the name *biotite* cannot be justifiably applied to the clay mineral for the same reasons as those which led Grim, Bray, and Bradley (5) to reject muscovite as a name for the dioctahedral clay mica. Thus, the manner of occurrence of the Scottish mineral, for example, suggests that it is not formed simply by the mechanical disintegration of ordinary biotite (see below). In spite

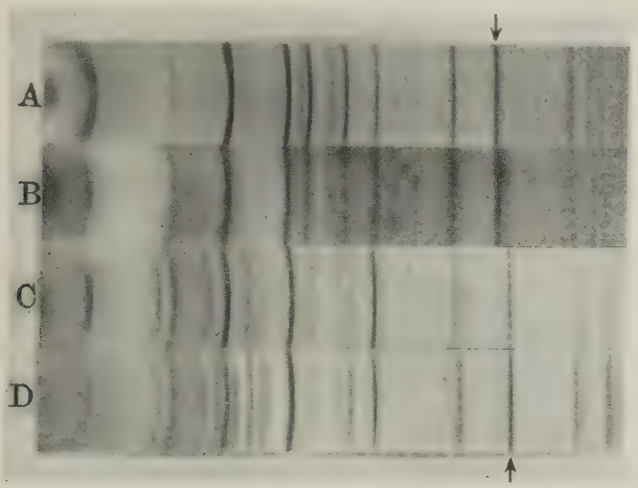

FIG. 1. X-ray powder diffraction photographs of: A, biotite, Glen Buchat, Aberdeenshire; B, the trioctahedral clay mica, Balquhain, Aberdeenshire (this clay was heated at 700° C. to eliminate kaolinite lines); C, dioctahedral illite, Ballater, Aberdeenshire; D, muscovite, Goshen, Massachusetts. (Arrows indicate positions of (060) lines.)

of these difficulties, however, it is not proposed to introduce a new mineral name at this time, since it is felt that this would be likely merely to add to the existing confusion in the nomenclature of the clay micas, especially since data on the trioctahedral clay mica itself are still rather scanty.

[1] Through the kindness of Professor Sven Gavelin of Stockholm and Dr. B. Collini of Uppsala I have been able to take X-ray powder photographs of a sample of Nordenskiöld's material from Taberg, Sweden. Although it has the appearance of an altered mica this material gives the powder pattern of a trioctahedral montmorillonite, indicating that it consists of an aggregate of montmorillonite crystallites pseudomorphous after mica. The degree of alteration of Nordenskiöld's material, however, probably varies in different parts of his samples since his optical and chemical data suggest that the material which he himself examined may have been less highly altered than the sample examined by the present writer.

The weathering of the trioctahedral mica.

(*a*) *The vermiculitic product.*—X-ray photographs of the soil-clays show the 'clay biotite' in various stages of decomposition, but seldom in the unweathered condition. Out of some hundreds of soil-clays examined it occurs fresh in only a few cases and then at the bottoms of the profiles in the relatively unweathered parent material horizons. More normally, it occurs as a mixed-layer structure with vermiculite to which it breaks down readily under a wide range of conditions, the process of breakdown approximating to the breakdown of macroscopic biotite into vermiculite in the sand fractions of the soil (8). In many cases, the process of decomposition can be traced upwards through successive layers of the profiles, from the unweathered or nearly unweathered condition of the mineral at the bottom of the profile to its vermiculitic weathering product in the surface layers. The process is best followed in a virgin profile which has not been subjected to cultivation.

Initially, the decomposition process is seen as a broadening of the first-order basal reflection at 10 Å., and in some photographs a tendency for this reflection to tail off on the low-angle side is observed. The intermediate stages of the process are characterized by the presence of diffraction bands stretching from 10 Å. to 14 Å. on the photographs and corresponding to varying numbers of 10 Å. and 14 Å. mixed layers. Sometimes the bands are of uniform intensity and have well-defined edges; more commonly they consist of two diffuse peaks at 10 Å. and 14 Å. with a region of minimum intensity between. Nowhere has there been found a single reflection at 11·5 Å. or 12 Å. such as occurs in hydrobiotite, the mixed-layer mineral described by Gruner (9) which consists of approximately equal numbers of mica and vermiculite layers.

The 14 Å. reflection of these clays is not displaced to 17·7 Å. on treatment with glycerol (10) so that it cannot be due to montmorillonite; and its replacement by a line at 9–10 Å. after heating at 500° C. for a number of hours indicates that the 14 Å. mineral is a vermiculite rather than a chlorite. The displacement of the 14 Å. reflection to 10·5 Å. on saturating the clay with ammonium ions confirms the identification, since this reaction is found to occur with vermiculites but not with chlorites (11, 12). It is plain that these soil-clays do not contain appreciable amounts of chlorite, but the possibility of the presence of relatively small numbers of chlorite layers occurring interleaved with vermiculite layers cannot be dismissed.

As in the weathering of macroscopic biotite (8), the weathering process of the trioctahedral clay mica consists first of all in the loosening of the attractive forces binding the 10 A. mica layers together, followed by the taking-up of double layers of water molecules between each pair of alumino-silicate layers. When this process is complete the mineral is a vermiculite and gives a strong (002) reflection at 14 Å. (table II).

TABLE II. X-ray diffraction diagrams of the weathering products of the trioctahedral clay mica (Fe-$K\alpha$).

1.		2.	
d Å.	$I_{est.}$	d Å.	$I_{est.}$
14·1	10	17·8	10 b
4·9	2	9·0	3 d
4·59	2	4·56	5 d
3·51	4	4·20	
3·18	1	3·66	2
2·93	1	3·0	1 d
2·71	1	2·56	4 d
2·63	4	2·44	4
2·44	4	1·70	0·5
1·530	6	1·532	5
1·32 / 1·28	2 d	1·31	1 d

b = broad; d = diffuse.

1. Vermiculitic product.
2. Montmorillonitic product (glycerol-saturated).

In the decomposition of macroscopic biotite into vermiculite a certain stage occurs at which a *single* layer of glycerol molecules can be introduced between the alumino-silicate layers causing the expansion of the lattice from 10 Å. to 14 Å. to take place prematurely (8), and the same reaction is found to occur during the decomposition of the 'clay biotite'. In most of the soil-clays partially decomposed (and potentially-expanding) layers of the 'clay biotite' as well as unweathered layers and vermiculite layers exist together, so that the addition of glycerol to the clay usually causes the expansion of a proportion of the 10 Å. layers. This is seen on the diffraction photographs as an enhancement of the 14 Å. reflection relative to the 10 Å. if separate 10 Å. and 14 Å. reflections were originally present (fig. 2 B); or if a band of more or less uniform intensity was present at 10–14 Å. before treatment, the intensity in the 14 Å. region becomes relatively stronger and a sharp 14 Å. reflection may be resolved (fig. 2 C). In the early stages of decomposition, there may be no 14 Å. line perceptible till after glycerol saturation (fig. 2 A); on the other hand, at a sufficiently advanced stage of decomposition all the layers will have expanded to 14 Å. by natural means,

and in this event addition of glycerol causes no further change (fig. 2 D).

(*b*) *The montmorillonitic product.*—Although the weathering product of the 'clay biotite' is normally a vermiculite, under certain conditions

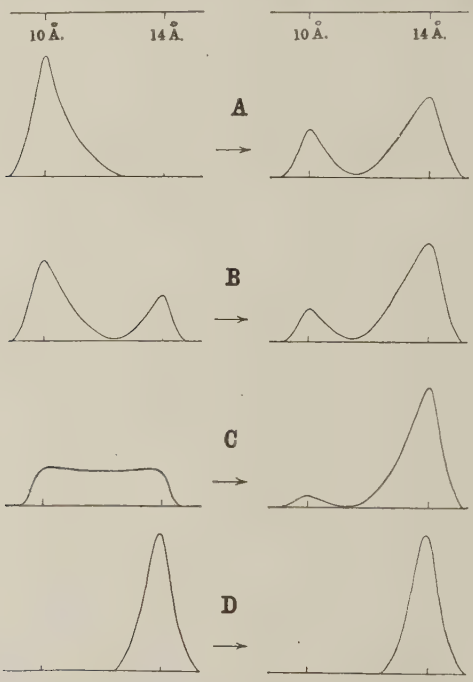

FIG. 2. The effect of glycerol treatment on the shapes of the 10 Å. and 14 Å. reflections at various stages during the breakdown of the trioctahedral clay mica into vermiculite (diagrammatic).

A. Glycerol treatment causes a 14 Å. reflection to develop with a corresponding reduction in the intensity of the 10 Å. reflection.

B. The intensity of the 14 Å. reflection increases relative to that of the 10 Å. after treatment.

C. A sharp 14 Å. reflection is resolved from a 10–14 Å. band by the treatment.

D. An already fully-developed 14 Å. reflection is unaffected by treatment.

the breakdown proceeds directly to the formation of a trioctahedral mineral with a freely-expanding lattice like montmorillonite.[1] Two conditions seem to be necessary for the formation of this product, since it occurs only in soils: (i) derived ultimately from basic or ultra-basic rocks; and (ii) under poor drainage conditions, that is, where the soil

[1] The diffraction pattern of this material resembles that of the sample of Nordenskiöld's pholidolite examined by the writer.

remains below the level of the water-table for long periods of the year. Saturation of this mineral with glycerol leads to the taking-up of a double layer of glycerol molecules giving the strong 17·7 A. reflection typical of glycerol-montmorillonite (10) (table II). In its natural state the mineral gives a diffraction pattern showing a weak and indefinite band at 10–16 A. or thereabouts in place of a sharp basal reflection, suggesting pronounced variation in the numbers of water layers between successive alumino-silicate layers. In appearance this slight hazing of the photograph is quite unlike the relatively well-defined 10–14 Å. band which forms during the alteration of the 'clay biotite' into vermiculite, and its reaction to glycerol treatment is also quite distinct.

Both the conditions mentioned above appear to be necessary for the development of the montmorillonitic product of weathering; if only one holds, the weathering product is vermiculite. Thus, vermiculite forms from the 'clay biotite' in soils of intermediate or acid origin irrespective of the drainage conditions, and also in the more freely-drained soils of basic origin. In certain basic soils where the lower layers are more or less normally waterlogged while nearer the profile surface freer drainage conditions exist, the montmorillonitic weathering product present in the lower layers gives way to the vermiculitic product in the surface layers, and both may coexist in the intermediate layers.

(*c*) *Rate of breakdown.*—The rate at which the trioctahedral clay mica breaks down in the soil is a notable feature. As has been already indicated, considerable searching was required before a clay was found which gave a single sharp basal reflection at 10 Å. which was not affected by glycerol treatment. Compared with its dioctahedral analogue illite, the trioctahedral mineral decomposes rapidly, although Nagelschmidt (13) has suggested that the former mineral is also unstable under humid temperate conditions. According to Nagelschmidt, as illite alters, the 10 Å. reflection tends to form a 'tail' extending towards low angles and the first well-defined product of its breakdown is a montmorillonite, a process of breakdown very similar to that found with the trioctahedral clay mica under the special circumstances defined above. On the other hand, no parallel to the more usual breakdown of the trioctahedral mineral into vermiculite with its comparatively definite steps seems to occur with the dioctahedral clay mica.

The removal of free oxides from the clays.

When examining soil-clays by X-ray methods it is often advantageous to remove the free iron and aluminium oxides which form amorphous

coatings round the crystalline particles and cause general scattering of the X-ray beam, and several excellent methods of achieving this are available. It is advisable, however, to use such chemical treatments with care since they may lead to misinterpretations if the clays concerned are vermiculite-bearing. The replacement of the exchangeable magnesium ions which are normally present in vermiculite by other ions has been shown to cause changes in the structure of the water layers and hence in the position of the basal reflections on the diffraction photographs (11, 14). Thus, if an iron-removal treatment involving (say) an ammonium salt is used, the basal spacing of any vermiculite layers present may be wholly or partly displaced to about 10·5 Å. It is important, therefore, to determine the effect of such chemical treatments on the positions of the basal lines of a pure specimen of vermiculite before employing them on soil-clays suspected of containing vermiculitic minerals.

Chemical and cation-exchange data.

So far it has not been possible to isolate the 'clay biotite' or its weathering products from each other or from the kaolinite with which they are associated in the soil-clays,[1] and until this is effected detailed optical examination of the minerals must be foregone (15). For the same reason chemical and cation-exchange determinations on the pure minerals cannot be made directly. Another difficulty lies in the readiness with which the 'clay biotite' decomposes in the soil, a factor which at present makes it extremely difficult to decide whether the mineral is completely fresh in a given sample.

An attempt has been made to determine the approximate composition of the 'clay biotite' by recalculating the analysis of a clay in which the 10 Å. reflection is comparatively strong and sharp and unaffected by glycerol treatment, indicating that the mineral is in a fresh or fairly fresh condition. It has been shown, however, that during decomposition in the soil the chemical composition of ordinary biotite alters considerably before much change is observed on the X-ray diagram (8), and it is probably correct to assume that this is also true of the clay mineral. The presence of a 10 Å. reflection is therefore no guarantee that the mineral has not altered chemically to some extent, and the

[1] X-ray photographs of clay sub-fractions separated by means of the super-centrifuge failed to reveal any pronounced tendency for the trioctahedral minerals to concentrate in a particular size fraction.

ow alkali and very high water contents obtained (table III) suggest hat it has in fact done so.

TABLE III. Chemical analysis (recalculated to allow for impurities) and atomic composition of the trioctahedral clay mica (calculated on the basis of OH = 8, O = 40).

SiO_2	40·87	Si	13·20	16
Al_2O_3	20·45	Al	2·80	
		Al	4·97	11·89
TiO_2	2·13	Ti	0·53	
Fe_2O_3	12·81	Fe^{+3}	3·06	
MgO	6·86	Mg	3·26	
MnO	0·25	Mn	0·07	
CaO	0·89	Ca	0·31	2·05
K_2O	3·25	K	1·33	
Na_2O	0·70	Na	0·41	
H_2O+ (105–300° C.)	4·94	OH	8	48
H_2O- (300° C.)	6·90	O	40	
	100·05			

Comparison with standard X-ray photographs of artificial mixtures f mica and kaolinite indicates that 35 % (±5 %) kaolinite is present the analysed clay, and the figures in table III have been arrived at fter allowing for this amount. Treatment of the clay with sodium ydrosulphite (16) extracted 7·50 % 'free' Fe_2O_3, and this has also been ken into account; amorphous alumina and silica, on the other hand, ere negligibly small. The amounts of water released on heating at 05° C. and at 300° C. were determined after removal of the free iron xides. The proportion of water and hydroxyl actually associated with e trioctahedral mica is, however, uncertain, and the atomic composion given in table III has therefore been calculated on the basis of H = 8, O = 40. The percentage of ferrous iron is also unknown since e small amount of organic matter remaining in the soil-clay even after peated peroxide treatments interfered with its determination.

In view of the foregoing it is clear that the analysis quoted in ble III may be regarded at best as no more than a rough approximaon to the true composition of the trioctahedral clay mica. It has been cluded here simply because anything closer than a rough approximaon will be difficult to obtain until a method of isolating the mineral available. It is clearly essential to keep the limitations of the analysis mind in any comparison with other mineral analyses.

The cation-exchange capacity of the analysed clay was determined fter removal of the free iron oxides. After making allowance for the olinite constituent and neglecting the effect of the inorganic amor-

phous component, the exchange capacity of the 'clay biotite' is found to be about 40–50 m. equiv. per 100 g. of clay, although it is possible that a somewhat lower value would be obtained if the mineral was completely fresh. Similar determinations on the vermiculitic and montmorillonitic products of weathering indicated an exchange capacity in the region of 100 m. equiv. per 100 g. in both cases.

Field relations.

The soils of the area belong to the Large Podzol Zone and are in the main members of the Grey-Brown and Brown Podzolic Sub-zones (17). They are developed on glacial drift laid down some 10,000–20,000 years ago, and although there has been a certain amount of mixing of parent-material types, in general the soil-types are clearly distinguishable in the field. Soil-clays from a wide range of parent-material groups have been surveyed including parent materials ultimately derived from acidic, intermediate, basic, and ultrabasic igneous rocks, from quartzose- and mica-schists, slates, mudstones, sands, and gravels, and red clay.

In the clay fractions of these soils the trioctahedral clay mica and its weathering products are widespread and frequently make up half or more of the crystalline component. The amounts of these minerals in the clays appear to bear no relation whatsoever to the amount of biotite in the rocks from which they are derived; and it is, as a consequence, improbable that the 'clay biotite' is a residual mineral produced by the disintegration and degradation of the original biotites of the parent rock, but rather that it is formed as an authigenic mineral in the soil-clays. The presence of the 'clay biotite' itself in the clay fraction of a given soil is, moreover, not incompatible with the coexistence of vermiculite flakes in the sand fraction of that soil, the latter material having been formed by the decomposition of macroscopic biotite.

The weathering changes in the trioctahedral clay mica are easily followed on the diffraction photographs from the positions and shapes of the basal reflections. The initial identification of the mineral and its decomposition products is, however, not always straightforward in the presence of other clay minerals. Thus, the important (060) line (or (06) line in the case of the montmorillonitic member) of the trioctahedral minerals coincides with a quartz line at 1·53 Å. so that the presence of quartz is a distinct hindrance to their identification. If this mineral is present, comparison of the relative intensity of the 1·53 Å. line with the 1·81 Å. and 1·37 A. lines of quartz which are of the same intensity may indicate whether the first of these lines is wholly due to the quartz

or not; but the exclusion of quartz from the sample by selecting a finer size fraction may be necessary. The majority of the soil-clays examined during this investigation show no sign of quartz in the fraction $< 1{\cdot}4\ \mu$ equivalent spherical diameter, and even in those clays derived from quartz-bearing rocks the amount of quartz present is either negligible or very small in this size fraction, so that at most only the strongest quartz line at 3·35 A. is visible on the diffraction photographs.

In several of the soil-clays, dioctahedral illite coexists along with the trioctahedral minerals and kaolinite, and at one locality in Aberdeenshire (Ordley) it makes up 70 or 80 % of the crystalline material, the other 20–30 % consisting of kaolinite and haematite. With this single exception all the localities in the north-east of Scotland examined so far have shown evidence of appreciable amounts of the 'clay biotite' and/or its weathering products. It is interesting to note that we have also found minerals of this type in soil-clays from the south and west of Scotland, and from Northern Ireland.

In conclusion, it may be noted that the difficulty of distinguishing the 'clay biotite' from its dioctahedral analogue by means of X-rays in the presence of other clay minerals and quartz suggests the possibility that the two micas may have been confused in the past. Similarly, the distinction between vermiculite and montmorillonite is a fine one and, before the glycerol method for the positive identification of the latter mineral (10) was developed, it is probable that it was not always made, since the usual heating test quoted in the literature for confirming the presence of montmorillonite would not eliminate vermiculite (viz. displacement of the 14 Å. line to 10 A. after heating the sample at 500° C. for several hours). The high cation-exchange capacity possessed by vermiculite and unsuspected until recently (14) would also tend to cause its confusion with montmorillonite.

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An X-ray examination of a sample of pure calcite and of solid-solution effects in some natural calcites.

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Introduction.

In the course of the routine X-ray examination of a number of low-grade iron ores in order to determine their constitution, it was observed that the calcite phase had varying interplanar spacings. Since these variations could have been due to differing solid-solution contents of other carbonates, further consideration was given to this point. The existence of these generally small amounts of solid solution is of some technological interest.

A sample of 'specpure' calcite, supplied by Messrs. Johnson, Matthey & Co. Ltd., was used to provide accurate lattice parameters and interplanar spacings for pure calcite. There was no satisfactory list of interplanar spacings available with the desired accuracy, although for ordinary identification purposes the values supplied in the 'Index of X-ray diffraction data' (Amer. Soc. Testing Materials) are adequate. Part I of the present paper discusses the results obtained from this 'specpure' calcite in relation to previously reported values of the rhombohedral angles α and α' and the interplanar spacing of the cleavage plane. Part II describes the examination of the solid-solution effects referred to in calcites from seven samples of iron ore and in two other natural calcites. An interpretation of the results is attempted.

Part I. Lattice parameters and interplanar spacings of pure calcite.

A sample of calcite of high purity was obtained from Messrs. Johnson, Matthey & Co. Ltd. The manufacturer's report on this 'specpure' compound is contained in Appendix I together with details of two other calcites. Powder photographs were taken with both Co-$K\alpha$ and Cu-$K\alpha$ radiations in the 19 cm.-diameter camera. The final values for the lattice parameters were obtained from the Cu-$K\alpha$ photograph. The lattice parameters were used in the calculation of accurate interplanar

spacings which are given in table I. These spacings have been submitted for inclusion in a new supplement of the 'Index of X-ray diffraction data' (A.S.T.M.). Hexagonal indices are listed in table I as these are generally more convenient. The pattern obtained with cobalt had lines

TABLE I. Lattice parameters and interplanar spacings of pure calcite.

a_{rh} 6·3748±0·0005 Å. α 46° 4·8′ (46·08°)

a_{hex} 4·9898±0·0003 Å
c_{hex} 17·060±0·005 Å. } at 18° C.

d in Å.	*I.*	*hkil.*	*d* in Å.	*I.*	*hkil.*
3·855	w	$10\bar{1}2$	0·9897	vw	$32\bar{5}1$
3·035	vs	$10\bar{1}4$	0·9876		$40\bar{4}7$
2·843	vw	0006	0·9848	wm	$32\bar{5}2$
2·495	wm	$11\bar{2}0$	0·9807	w—	$31\bar{4}10$
2·285	m	$11\bar{2}3$	0·9775	wm	$10\bar{1}17$
2·095	m	$20\bar{2}2$	0·9767		$21\bar{3}14$
1·9274	w	$20\bar{2}4$	0·9656	w+	$32\bar{5}4$
1·9123	ms	$10\bar{1}8$	0·9637	m—	$40\bar{4}8$
1·8753	ms	$11\bar{2}6$	0·9562	vw	$20\bar{2}16$
1·6259	w	$21\bar{3}1$	0·9520	vvw	$32\bar{5}5$
1·6042	m	$21\bar{3}2$	0.9430	m—	$41\bar{5}0$
1·5868	vw	$10\bar{1}10$	0·9377	wm	$22\bar{4}12$
1·5253	m -	$21\bar{3}4$	0·9183	vw	$32\bar{5}7$
1·5178	vvw	$20\bar{2}8$	0·8990	w	$32\bar{5}8$
1·5093	w	$11\bar{2}9$	0·8951	vw	$41\bar{5}6$
1·4732	w	$21\bar{3}5$	0·8928	wm—	$21\bar{3}16$
1·4598	vvw	$10\bar{1}11$	0·8926		$30\bar{3}15$
1·4404	m	$30\bar{3}0$	0·8865	wm	$40\bar{4}11$
1·4217	wm	00012	0·8860		$11\bar{2}18$
1·3568	w	$21\bar{3}7$	0·8599	vw	$50\bar{5}2$
1·3389	w+	$20\bar{2}10$	0·8572	w—	$32\bar{5}10$
1·2967	wm	$21\bar{3}8$	0·8550	w—	$21\bar{3}17$
1·2850	vvw	$30\bar{3}6$	0·8470	w	$50\bar{5}4$
1·2475	w	$22\bar{4}0$	0·8369	w+	$10\bar{1}20$
1·2352	m –	$11\bar{2}12$	0·8316	w	$33\bar{6}0$
1·1798	m—	$21\bar{3}10$	0·8129	wm	$42\bar{6}2$
1·1538	m+	$31\bar{4}4$	0·8124		00021
1·1423	wm	$22\bar{4}6$	0·8084	vvw	$40\bar{4}14$
1·1247	vw	$21\bar{3}11$	0·8021	w+	$42\bar{6}4$
1·0614	vw	$20\bar{2}14$	0·8010		$50\bar{5}8$
1·0473	wm	$40\bar{4}4$	0·7982	w	$33\bar{6}6$
1·0448	m	$31\bar{4}8$	0·7966	m—	$31\bar{4}16$
1·0352	w—	$10\bar{1}16$	0·7934	w—	$20\bar{2}20$
1·0349		$11\bar{2}15$	0·7918	vvw	$30\bar{3}18$
1·0230	vvw	$21\bar{3}13$	0·7910	vvw	$32\bar{5}13$
1·0118	m+	$30\bar{3}12$	0·7858	s	$41\bar{5}12$
			0·7753	vw	$51\bar{6}1$

The above spacings are reported in Ångström units, but in the earlier work of Krieger and others the unit is that now referred to as kX. The necessary conversion from the above values to kX units has been effected before using the spacings in fig. 1 and elsewhere.

as far as and including $32\bar{5}7$, but $32\bar{5}8$ may appear on films from some cameras. The actual parameter values obtained were:

a_{rh} 6·3748±0·0005 Å. = 6·3619 kX, α 46° 4·8′ (46·08°), at 18° C.

Referred to hexagonal axes, these values correspond to:

$$a_{\text{hex}}\ 4{\cdot}9898 \pm 0{\cdot}0003\ \text{Å.} = 4{\cdot}9797\ \text{kX},$$

$$c_{\text{hex}}\ 17{\cdot}060 \pm 0{\cdot}005\ \text{Å.} = 17{\cdot}026\ \text{kX},$$

with $c/a = 3{\cdot}4190$.

Dr. A. J. C. Wilson of University College, Cardiff, kindly examined this sample of calcite by the same method and obtained parameter values very close to our own, exact agreement being reached with copper radiation as regards the value of the rhombohedral angle α, although our own photograph with cobalt radiation suggested a slightly lower value.

The new data obtained may be compared with previously reported values for the various lattice parameters and the rhombohedral angle α. It should be mentioned that the X-ray unit cell to which the above measurements refer is the one described by Dana as $M(40\bar{4}1)$, so that his cleavage rhombohedron $r(10\bar{1}1)$ becomes $(10\bar{1}4)$. The angle between two faces of this cleavage rhombohedron, denoted by rr', is of interest in optical goniometry, and values of this angle have therefore been calculated for comparison with each other, and with the accepted value of 74° 55′. If the cleavage rhombohedron itself is regarded as a unit cell, the interaxial angle is in the region of 101° 54′, and values of this angle, which we denote by α', have been reported by other workers. It is therefore of interest to compare these various angles as well as the corresponding lattice parameters (in kX units). The following values have been obtained:

	a_{rh}.	α.	a_{hex}.	c.	c/a.	α'.	rr'.
Bragg[1], 1914 ...	6·361	46° 7′	4·982	17·019	$3{\cdot}417_3$	101° 55′	74° 55′
Bearden[2], 1931 ...	—	46° 4′ 42″	—	—	3·4191	101° 54′ 4″ ±10″	74° 56′ 31″
Du Mond & Bollman[3], 1936 ...	(6·3593)	46° 5′	(4·9871)	(17·019)	3·4186	101° 54′ 18″ ±48″	74° 56′ 12″
New data, 1949 ...	6·3619	46° 4′ 48″	4·9797	17·026	3·4190	101° 54′ 9″	74° 56′ 24″

The agreement between the last three sets of values for c/a, α', and rr' is very close and may be regarded as satisfactory. The present value of 6·3619 kX for the rhombohedral cell edge is not markedly higher

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[2] J. H. Bearden, Phys. Rev., 1931, vol. 38, p. 2089.
[3] J. W. M. Du Mond and V. L. Bollman, Phys. Rev., 1936, vol. 50, p. 524.

than the early determination of 6·361 by Bragg. The parameter values in brackets from Du Mond and Bollman are calculated from the rather low value of the spacing referred to below.

There have been a number of reported values for the interplanar spacing of the $10\bar{1}4$ planes, referred to above, as corresponding to the faces of the cleavage rhombohedron. This distance was of great importance in the determination of standard X-ray wave-lengths. As explained by Compton and Allison,[1] if the diminishing effect of refractive index with increasing order of diffraction is taken into account, Siegbahn's value of 3·02904 kX (at 18° C.) approaches a true value of 3·02945 kX. Our own value is $3{\cdot}0294_1$ kX and would, as it is uncorrected for refraction, approximately correspond to the value given by Compton and Allison for the fourth order, viz. $d_4 = 3{\cdot}02942$. Y. C. Tu[2] obtained 3·0294 for this spacing, although Du Mond and Bollman, using a powder method, obtained 3·02923 kX. It is not easy to account for this last-named result being relatively lower than the others, but it should be noted that the three values of α' which were determined showed a rather wide scatter, which gives a correspondingly marked $\pm$ error on the value of d. Again, these authors used a sample of natural calcite which could conceivably be affected by very slight traces of solid-solution elements as suggested below.

Part II. Solid-solution effects in some natural calcites.

Description of samples examined.—The calcites examined are listed in table II. No. 1 is a fine-grained limestone and no. 2 a large crystal obtained from a lead mine in North Wales. Nos. 3 to 6 are calcites separated from certain low-grade iron ores by a simple gravity-settling method. The separation was not expected to be complete and, as suggested in table IIb, there are small amounts of chalybite and goethite, and occasionally other constituents. These do not affect the measurements of the calcite lines on the X-ray powder photographs except for one or two instances of overlapping lines. The small amounts of sample normally produced were not sufficient for a complete chemical analysis and a choice had to be made as to the most desirable quantities to determine. As a consequence some uncertainties arose, e.g. in regard to the amount of calcium present as calcium phosphate. In the case of the samples nos. 7 and 8 the calcite spacings were measured on

[1] A. H. Compton and S. K. Allison, X-rays in theory and experiment. 1936, pp. 680–682.

[2] Y. C. Tu, Phys. Rev., 1932, vol. 40, p. 662.

TABLE IIa. Chemical data for calcites and ores.

Ref. No.	Description of Material.	Weight percentages. CaO.	CO_2.	total Fe.	MnO.	MgO.	P_2O_5.	Molecular ratios $\frac{\text{wt.\%} \times 100}{\text{molecular wt.}}$ CaO.	MnO.	MgO.	FeO.	CO_2.	P_2O_5.	$Ca_3P_2O_8$.
1.	Limestone from Hope (Derbyshire)	53·95	42·2	0·31	0·01	1·12	—	96·19	0·014	2·78	>0·55	96·0	—	—
2.	Calcite from North Wales	55·7	43·7	0·19$_5$	0·10	0·60		99·31	0·141	1·49	>0·35	99·0	—	—
3.	Calcite from Frodingham ironstone (a)...	24·7	21·2	33·0	1·13	4·68		44·04	1·59	11·61	>2·37 (?)	48·0	—	—
4.	Calcite from Frodingham ironstone (b)...	37·05	38·7	14·6	1·55	3·81		65·97	2·19	9·45	10·4 (?)	88·0	—	—
5.	Calcite from Yarboro' (Lincs.) (a)	41·55	33·4	8·57	0·60	2·42	—	74·08	0·85	6·00	>1·07 (?)	76·0	—	—
6.	Calcite from Yarboro' (b)	41·55	30·75	13·0	0·59	5·32		74·08	0·83	13·2	(?)	70·0	—	—
7.	Ore from Scunthorpe (a)	30·16	26·10	FeO 3·89	0·89	1·08	0·77	53·77	1·25	2·7	5·4	59·0	0·54	52·15
8.	Ore from Scunthorpe (b)	14·0	18·26	FeO 14·33	0·87	2·06	0·99	24·96	1·23	5·11	19·9	41·5	0·67	22·95
9.	Raw Trent ore (Lincs.) (Calcite separated for photograph)	22·32	22·27	FeO 9·13	2·06	2·43	1·03	39·79	2·90	6·03	12·7	50·5	0·72	37·63

TABLE IIb. X-ray results and data deduced from Table IIa.

No.	Description of Material.	$\frac{MnO \times 100}{CaO + MnO}$.	$\frac{MnO \times 100}{CaO + MnO + FeO}$.	$\frac{MnO \times 100}{CO_2}$.	$\frac{MnO \times 100}{CO_2 - 2MgO}$.	Mean % change in calcite = $100 \times \Delta d_2/d$.	Constituents other than calcite.
1.	Limestone from Hope (Derbyshire)	0·014	0·015	0·015	0·015	0·085	—
2.	Calcite from North Wales	0·14	0·14	0·14	0·147	0·13	—
3.	Calcite from Frodingham ironstone (a)	3·61	3·30	3·54	6·40	0·30	$FeCO_3$ & goethite, small amount; dolomite, possible small amount
4.	Calcite from Frodingham ironstone (b)	3·20	2·49	2·49	3·17	0·24	$FeCO_3$, med./small amount; dolomite, ? very small amount
5.	Calcite from Yarboro' (Lincs.) (a)	1·12	1·12	1·12	1·32	0·20	$FeCO_3$, very small amount
6.	Calcite from Yarboro' (b)	1·11	1·19 (max.)	1·18	1·91	0·15	$FeCO_3$ & goethite, traces; dolomite, very small amount
7.	Ore from Scunthorpe (a)	2·33	2·07	2·12	2·33	0·30	$FeCO_3$, very small amount; goethite, small + amount
8.	Ore from Scunthorpe (b)	5·07	2·73	2·96	3·93	0·40	$FeCO_3$, medium amount; goethite, small/med. amount; Chamosite, possible small amount
9.	Raw Trent ore (Lincs.) (Calcite separated for photograph)	7·12	5·24	5·74	7·54	0·32	$FeCO_3$, small + amount; goethite, small + amount

photographs of the original iron ores for which more complete chemical analyses were available. In the last iron ore in the list, no. 9, the same analytical details were available, but the calcite from which the spacing measurements were taken was again largely separated from the other constituents. Further samples showing the same effect have been examined but are not reported as no chemical data is available.

In addition to the chemical analyses (weight percentages) table IIa also records the values of the 'molecular ratios' $\frac{(\text{weight percentage} \times 100)}{(\text{molecular weight})}$ of the various components. It was not possible in every case to decide how much of the 'total Fe' should be allocated to FeO, but in some instances this cannot be very much, whilst for nos. 7, 8, and 9, FeO was determined directly.

X-ray examination of calcite phase.—In considering the relation of the solid-solution effects observed in the calcite phase to the amounts of manganous oxide and other components it was necessary to measure the change in interplanar spacings themselves, since extrapolated values of the lattice parameters could not have been obtained in most of the cases examined owing to the weakness and diffuseness of the 'high angle' lines. A quantity representing the average decrease in interplanar spacings and thus of the lattice parameters was derived as explained in Appendix II. This was expressed as a percentage and represented by $\Delta d_2/d \times 100$. Thus, the standard interplanar spacings in table I were taken as correct and the effect of solid solution in the natural calcites was to lower the interplanar spacings by amounts which in proportion to the actual value of the spacing should have been more or less equal, assuming the axial ratio change to be negligible over the relatively small range of composition involved. The simple method of Appendix II gives the mean value of $\Delta d_2/d \times 100$ and allows for the absorption of the specimen in the powder camera. The quantity obtained is a measure of the amount of other carbonates in solid solution, and the actual values are recorded in table IIb.

Consideration of the available data.—The most probable elements replacing calcium in calcite solid solutions are manganese, iron, or magnesium. No X-ray data on the solid solutions formed between the various carbonates of these elements appear to have been reported apart from the work of Krieger[1] who tabulated interplanar spacings, densities, and also refractive indices of solid solutions between manganese and calcium carbonates, referred to as manganocalcites. Wayland, using optical and

[1] P. Krieger, Amer. Min., 1930, vol. 15, p. 23. [M.A. 4–274.]

density methods, reported complete solid solutions between these two end members.[1] Earlier, Ford had carried out an extensive study of minerals in the calcite group, and related densities and refractive indices to the composition of the various mineral samples examined.[2] This author suggested that manganese carbonate would be expected to dissolve to the largest extent, iron carbonate next, and magnesium carbonate the least, and that the solid solutions would probably be restricted. No extensive solid solutions of $FeCO_3$ or $MgCO_3$ in $CaCO_3$ have in fact been reported. Hawkes and Smythe[3] reported three calcites which appear to contain $FeCO_3$, $MgCO_3$, and $MnCO_3$ in solid solution. Smythe and Dunham[4] fitted these results into a ternary system $CaCO_3$–$MgCO_3$–$(Fe,Mn)CO_3$, but no other samples indicating a wide range of solid solutions in calcite were reported.

The small amounts of solid solution observed in the nine samples listed in table II could therefore probably be accounted for as being due to one or more of the three carbonates $MnCO_3$, $FeCO_3$, and $MgCO_3$. The samples did not lend themselves to density or to refractive-index measurements (apart from no. 2, which showed a very slightly higher value of ω than for pure calcite the difference being too small to be definitely related to the minor constituents). Consequently, the only standard of comparison from other work is the X-ray data of Krieger referred to above. These data are therefore taken as the basis on which the values of $\Delta d_2/d$ are related to the percentage solid solution of $MnCO_3$, assuming this is the main constituent in solid solution. This assumption may not be completely justified, but a good correlation with Krieger's work would tend to support it, and as suggested below this is in fact the case, although there is also some indication of the other possible solid-solution constituents.

Fig. 1 shows the variation with composition of Krieger's interplanar spacings for the first eight principal lines having the hexagonal indices shown. These points do not lie as consistently close to the straight lines drawn as might have been expected. The percentage of $MnCO_3$ in solid solution is taken direct in each case from the analysis given by Krieger, but there are also small amounts of $MgCO_3$ and $FeCO_3$, also in one sample $ZnCO_3$ and in another $SrCO_3$. If these minor constituents are allowed for the points are displaced slightly to the right, but by

[1] R. G. Wayland, Amer. Min., 1942, vol. 27, p. 614. [M.A. 9–124.]

[2] W. E. Ford, Trans. Connecticut Acad. Arts & Sci., 1917, vol. 22, p. 211. [M.A. 1–10.]

[3] L. Hawkes and J. A. Smythe, Min. Mag., 1935, vol. 24, p. 65.

[4] J. A. Smythe and K. C. Dunham, Min. Mag., 1947, vol. 28, p. 53.

amounts that are unimportant. The scatter of some of the points must be attributed to experimental error and, although straight-line variation is not necessarily followed, there is no reason for attempting to draw curves through the points available. These lines cut the vertical axis for zero $MnCO_3$ very near to the values for pure calcite from table I,

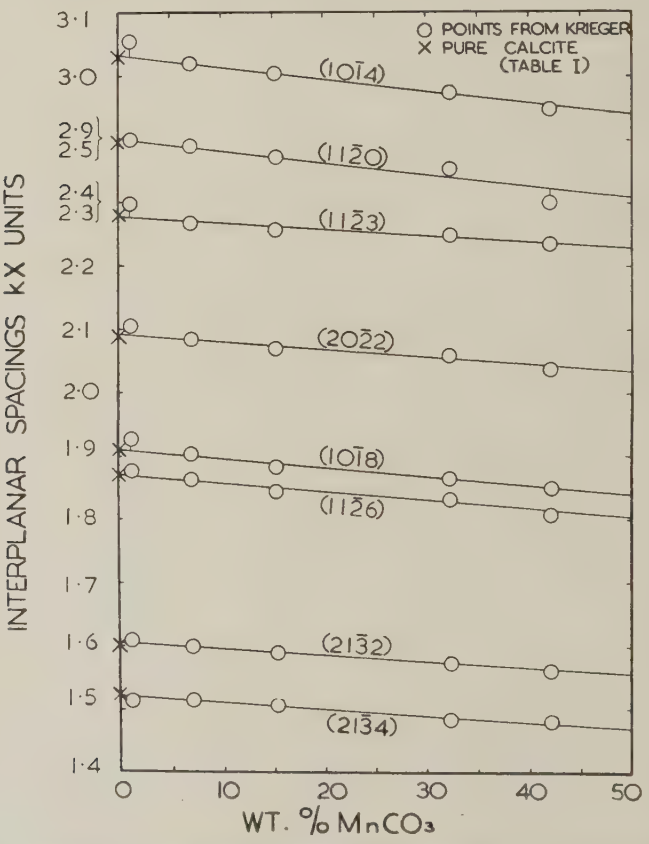

Fig. 1. Variation of interplanar spacings with composition for $CaCO_3$–$MnCO_3$ solid solutions. (Plotted from P. Krieger's data, 1930.)

converted to kX units, although it is noted that the first of Krieger's points (1·09 % $MnCO_3$) for several lines is somewhat high. Thus the value 3·055 kX for the 10$\bar{1}$4 line is very unlikely to be correct, as accurate values for pure calcite itself are all reported near to 3·03 kX.

The relative slopes of the lines in fig. 1 are different for different indices, but there is an average decrease of 3·15 % in terms of the

spacings for pure calcite on going from 0 to 50 % $MnCO_3$ by weight. This would correspond to 3·3 % decrease for a 50 atomic per cent. solid solution of $MnCO_3$. Thus our own average spacing decreases for solid solutions in calcite might be expected to lie near to a line of this slope

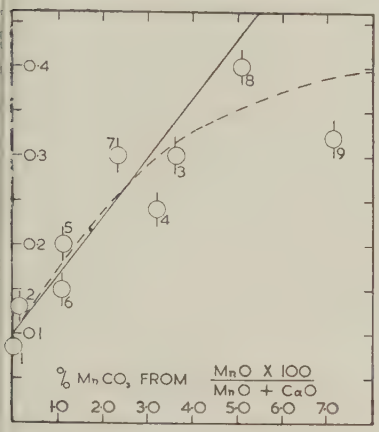

FIG. 2

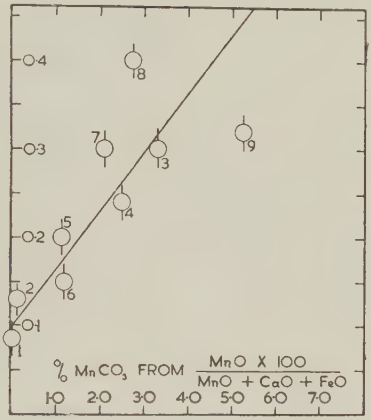

FIG. 3

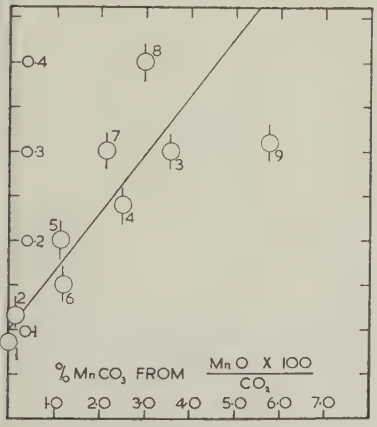

FIG. 4

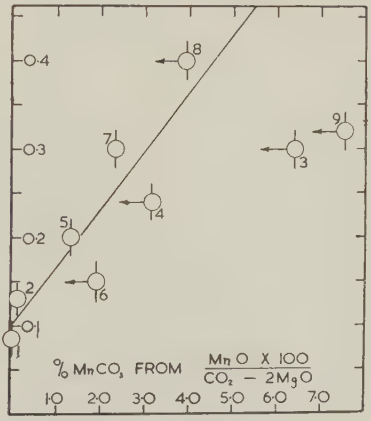

FIG. 5

FIGS. 2-5. Percentage decrease in interplanar spacings (ordinates) for calcite solid solutions. (The straight line on each figure has a slope equal to the average from Krieger's data.)

when plotted against some suitable quantity to represent % $MnCO_3$, providing that it is correct to account for most of the solid solution effect in this way.

In fig. 2 the % $MnCO_3$ is represented by $(MnO \times 100)/(CaO + MnO)$.

This ratio implies the assumption that all the CaO and MnO are combined as carbonate. Some of the samples, however, contained chalybite which may also have dissolved manganese carbonate, and in some cases the 'molecular ratio' for CO_2 table IIa is less than for the sum of the basic oxides (apart from MgO). Thus, some uncertainty in the use of the analytical data is bound to arise. In fig. 2 the points are scattered approximately on either side of the broken curve. A line of slope equal to 3·3 % decrease in 50 atomic % $MnCO_3$ is drawn to show how near the points correspond to this slope, which is suggested by Krieger's work.

Fig. 3 has a similar significance to fig. 2, but in cases where the FeO content is highest the points are shifted to the left. Thus, if the samples which contain a marked amount of chalybite also have some manganese carbonate dissolved in this constituent, it cannot be decided with certainty how much is so accounted for. The abscissae in fig. 3 are given by $(MnO \times 100)/(MnO + CaO + FeO)$, which divides the MnO in proportion to the relative amounts of the two carbonates where both are present. Some spacing changes in the chalybite constituent were in fact observed, but it was not possible to make any reliable quantitative estimates as for the calcite constituent, since iron was present only as a minor impurity in most cases.

In view of the inequality of the sum $MnO + CaO + FeO$, to which MgO may also be added, with the CO_2 content, it might seem better to express the % $MnCO_3$ in terms of the total carbonate, $(MnO \times 100)/CO_2$, as in fig. 4. If, however, the magnesium oxide is taken into consideration, the method of plotting must allow for its combination in the form of dolomite. This reduces the amount of carbonate as calcite. It is unlikely that all the MgO is combined as dolomite especially in those cases where the amount of MgO is highest. Fig. 5, therefore, which assumes all MgO as dolomite, has placed certain points too far to the right, the abscissae being $(MnO \times 100)/(CO_2 - 2MgO)$.

It is suggested that the best representation would lie between fig. 4 and fig. 5, but nearer the former. The points for nos. 7, 8, and 9 would be expected to be most affected in any of the methods of representation as the analyses are taken for the whole of the ore. In no. 5 the separation of the calcite has evidently not been as successful as for some of the others, but it falls very well in line with them, except in fig. 5 where the MgO content is effective in displacing it to the right. It is apparent that in all the four ways of representation the points are not widely scattered from a line of the slope suggested by the work of Krieger. This line does not, however, appear to pass through the origin—that

is assuming that it does not depart markedly from a straight line. The intercept may be significant, as it seems to suggest a small residual solid-solution content in natural calcites due to traces of some element or elements other than manganese.

The above results are based on the assumption that the 'specpure' calcite spacings are themselves the most correct available for the pure compound $CaCO_3$. The spectrographic examination of this calcite as carried out by the manufacturers is compared in Appendix I with a similar examination in our own laboratory of the calcite from North Wales, no. 2 in table II, and with a sample of 'A.R.' quality supplied as a laboratory chemical. The last of these is not referred to in table II as it is not a natural calcite and no ordinary analysis could be satisfactorily obtained. It is interesting, however, to observe that the percentage decrease in spacing is here 0·5. Thus, we have a chemically prepared pure calcite which appears to fall half-way between 'specpure' and the natural calcites examined as regards traces of solid-solution elements other than manganese. This intermediate position is obviously reflected in the results of spectrographic examination and it is significant that the elements chiefly concerned are iron and magnesium.

The intercept in figs. 2 5 which corresponds to a 0·1 % contraction of the lattice may thus be due to solid solution of traces of the elements iron and magnesium. The data in Appendix I suggest that iron is likely to be mainly responsible, as the 'A.R.' calcite shows considerably more iron relative to 'specpure', whereas the magnesium content, although greater than in 'specpure', has not increased so markedly. It must, however, be admitted that the presence of greater amounts of iron or magnesium in solid solution in some of the other samples is not ruled out. It can only be claimed that the above interpretation suggests that manganese is mainly responsible for the solid-solution effects observed in the natural calcites examined.

Finally, it is interesting to observe that the ionic diameter of manganese is nearest to that of calcium, and, as reported above, this is the only element whose carbonate seems to form a complete series of solid solutions with calcite. In contrast, both of the elements magnesium and iron appear to form a double carbonate in which the ions of calcium on the one hand and magnesium or iron on the other occupy, in an ordered arrangement, the lattice sites which in calcite solid solutions would be occupied in a random manner.[1] This does not exclude a limited mutual solid solution between chalybite or magnesite and calcite. It should be

[1] cf. W. L. Bragg, The atomic structure of minerals. 1937, p. 116.

added that Smythe and Dunham (loc. cit.) have pointed out that the solid-solution series between dolomite and ferrodolomite, in which some of the iron may be replaced by manganese, seems to terminate at about 75 % $(Fe,Mn)Ca(CO_3)_2$. It may be correct to suggest that complete solid solutions are favoured by ionic diameters which are not greatly different, whilst the dolomite type of compound is preferred if the difference becomes more marked.

Conclusions.—1. Accurate lattice parameters and interplanar spacings are given for a very pure sample of chemically prepared calcium carbonate. The values of the lattice parameters and of the rhombohedral angles α and α', the angle rr', and the $10\bar{1}4$ spacing (corresponding to the faces of the cleavage rhombohedron) are discussed in relation to previously published values, and agreement with the more recent determinations is considered to be very satisfactory.

2. X-ray examination of nine natural calcites of which seven are present in low-grade iron ores reveals changes in interplanar spacings which may be largely accounted for as being due to solid solution replacement of calcium by manganese. Four different methods of relating the X-ray measurements to the chemical data available all give general support to this view, although they are not all equally satisfactory representations, and there is no means of allowing for the fact that the calcite constituent could not be completely separated from other constituents. The results are in general agreement with the work of Krieger (loc. cit.) on manganocalcites. The amounts of other elements in solid solution may, however, be greater than implied by this agreement.

3. The presence of some iron and magnesium in solid solution as well as manganese is indicated, and there is evidence that the chemically pure calcite and a calcite of 'analytical reagent' quality are purer than any natural calcites. The natural calcites, including those listed by Krieger, suggest that, even with no manganese carbonate in solid solution, there is still a residual solid-solution content of some other carbonate or carbonates. This conclusion is supported by a spectrographic examination in which the calcite of 'A.R.' quality definitely falls between 'specpure' calcite and the naturally occurring calcites, especially as regards the iron and magnesium contents.

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Thanks are also due to Dr. A. J. C. Wilson who examined the 'specpure' calcite separately, and whose results generally confirmed our own.

APPENDIX I. Spectrographic examination of calcites.

The following table summarizes the data for 'specpure' calcite as reported by the manufacturer, and the corresponding data for two samples of calcite referred to in the text. The conditions of the tests for the two calcites were slightly different and so a pilot test on the 'specpure' was also carried out in our own laboratory.

Elements.	Lines detected.	'Specpure' manufacturer's report.	'Specpure' pilot test.	'A.R.' calcite.	North Wales calcite (no. 2 in table II).
Lead	2833·069 2802·003 2614·178	Faintly visible	Not detected	Barely visible	Barely visible
Strontium	4607·331 4077·714 3464·57	Faintly visible	Not detected	Visible	
Aluminium	3961·527 3944·032 3092·713 3082·155	Faintly visible	Faintly visible	Visible, slightly fainter than in N. Wales calcite	Visible, slightly fainter than in 'specpure'
Copper	3273·962 3247·540	Faintly visible	Faintly visible	Visible, stronger than in 'specpure'	Visible, fainter than in 'specpure'
Iron	3020·640 2599·396 2488·148 2483·270 2395·625 2382·039	Very faintly visible	Very faintly visible	The Fe lines detected too numerous to record individually, but all these lines were fainter than in N. Wales calcite	Fe lines too numerous to record individually
Silicon	2881·578 2516·123 2514·331 2506·899	Faintly visible	Faintly visible	Faintly visible, fainter than in 'specpure'	Faintly visible
Magnesium	3838·258 3829·350 2852·129 2802·695 2795·53 3096·899	Faintly visible	Faintly visible	Visible, stronger than in 'specpure'	Strongly visible
Silver	3382·891 3280·683	Barely visible	Barely visible	Faintly visible, stronger than in 'specpure'	Visible Faintly visible
Sodium	5895·923 5889·953 3302·988 3302·323	Very faintly visible (fainter than in graphite blank)	Faintly visible	Visible, stronger than in 'specpure'	Faintly visible
Manganese	4034·490 4033·073 4030·755 2949·205 2939·304 2933·063	—	—	—	Strongly visible
No lines of these elements were detected	—	As, Au, B, Ba, Be, Bi, Cd, Co, Cr, Ga, Ge, Hg, In, K, Li, Mn, Mo, Ni, Pt, Sb, Sc, Sn, Ti, Tl, V, W, Zn, Zr.	—	As, Bi, Be, Co, Cr, Cd, Mn, Mo, Ni, Sn, Sb, Ti, V, W, Zr, Zn.	As, Bi, Be, Co, Cr, Cd, Mo, Ni, Sn, Sr, Sb, Ti, V, W, Zr, Zn.

Conditions of test:

(*a*) 'Specpure' manufacturer's report:

A spectrographic examination was made by means of (i) an intermittent A.C. arc taking 7 amps., and (ii) a constant-current D.C. arc taking 5·6 amps., between pure graphite electrodes. In each case duplicate spectra of the sample and a comparison blank of the graphite were photographed with a flat-field medium-size spectrograph, on an Ilford long-range spectrum plate, the time of exposure being one minute.

(*b*) 'A.R.' (analytical reagent) calcite, North Wales calcite, and 'specpure' pilot test:

The spectrographic examination was made by means of an intermittent A.C. arc taking 6·5 amps., between pure graphite electrodes. The three spectra were photographed on to the same plate under the same conditions. (The wave-lengths are those listed in the Massachusetts Institute of Technology Wavelength Tables, 1939.)

Conclusions.—The 'A.R.' quality $CaCO_3$ appears to be slightly more impure than 'specpure', major differences being in Cu, Mg, Na, and most of all in Fe. The North Wales calcite contains Mg, Mn, and Fe as the chief impurity elements whilst there are also traces of Pb, Al, Cu, Si, Ag, and Na. The Mg and Fe contents both increase on going from 'specpure' to 'A.R.' and again on going from 'A.R.' to the North Wales calcite, whilst the last is the only one in which Mn has been detected. These conclusions are referred to in the text.

Appendix II. A method of obtaining the average lattice-spacing change for a non-cubic substance.

In cases where small solid-solution effects do not cause any marked axial ratio change the average change in interplanar spacings can be used to estimate the lattice-spacing change and hence the overall effect of the solid-solution replacement.

In our own practice the specimen in the powder camera is made large enough (corresponding to the absorption properties of the material) to ensure that most of the diffracted beam comes from the outer layers of the specimen. Under these conditions Jay[1] showed that a cubic substance would give an approximately linear extrapolation if lattice spacing is plotted against $\cos^2\theta/\sin\theta$. This function does, in fact, give points, very near indeed to the function $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ proposed by Taylor and Sinclair,[2] and by Nelson and Riley[3] for general use, and the extrapolated value is practically identical.

For a cubic substance we may write: $\Delta a/a = \text{const.}\times\cos^2\theta/\sin\theta$.

For a non-cubic substance the same kind of relationship must apply, and in this case the relative interplanar spacing difference $\Delta d/d$ is given by $\text{const.}\times\cos^2\theta/\sin\theta$. Thus $\Delta d/d\times\sin\theta$ gives a linear, or very nearly linear plot against $\cos^2\theta$. This method of plotting has the advantage that the quantity $\Delta d/d\sin\theta$ varies from zero to a finite value and $\cos^2\theta$ varies from 0 to 1, whereas if $\Delta d/d$ is plotted against $\cos^2\theta/\sin\theta$ both quantities increase indefinitely for $\theta\rightarrow 0$.

The straight line, or curve, obtained by plotting $\Delta d/d\sin\theta$ against $\cos^2\theta$ should pass through the origin for both quantities equal to zero. For the naturally occurring calcites examined this is not the case. The intercept from $\cos^2\theta = 0$ (i.e. $\sin\theta = 1$) gives a positive value for $\Delta d/d\sin\theta$. This implies that all the interplanar spacings

[1] A. H. Jay, Unpublished work. Referred to at conference of the X-ray Analysis Group (Institute of Physics) in 1942 and again in 1948.

[2] A. Taylor and H. Sinclair, Proc. Phys. Soc. London, 1945, vol. 57, p. 126.

[3] J. B. Nelson and D. P. Riley, Proc. Phys. Soc. London, 1945, vol. 57, p. 160.

have, in addition to the variable absorption (and eccentricity) correction a further difference relative to the standard interplanar spacings for the pure calcite: i.e. $\Delta d = \Delta d_1 + \Delta d_2$,

where Δd_1 = variable correction due to absorption, &c.

Δd_2 = spacing change due to solid solution.

$\frac{\Delta d - \Delta d_2}{d}$ would now give an almost linear plot against $\cos^2\theta$ passing through the origin.

$\frac{\Delta d_2}{d}$ (expressed as a percentage) gives the relative change in spacings due to elements replacing calcium in solid solutions. Since the values are all 'positive', the true interplanar spacings have decreased, suggesting the presence of ions of smaller size than calcium (of which manganese, iron, and magnesium are examples).